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February 8, 2021

Via E-Mail

Mark Garvey
Waste and Chemical Enforcement Division
Office of Civil Enforcement
United States Environmental Protection Agency
1200 Pennsylvania Ave NW (Mail Code 2249A)
Washington, DC 20460

Re: Second Response to TSCA Section 11 Request to Inhance Technologies dated January 14, 2021 (the "Information Request") relating to per and poly fluorinated substances ("PFAS") regulated under the Toxic Substances Control Act ("TSCA")

Dear Mr. Garvey,

As noted in our previous submittal, I have been engaged to assist Inhance Technologies LLC ("Inhance Technologies") with regard to its response to the above-referenced Request.

Per our discussion and your email of January 25, 2021, this letter accompanies Inhance Technologies' second partial response to the Information Request and addresses those matters requested in Section B of the Information Request. We understand that we will discuss the scope and timing of any necessary future submittals with you in more detail over the coming weeks.

As we have previously discussed, Inhance Technologies believes that its processes do not account for the levels and types of PFAS compounds identified in the PEER report on Anvil 10-10 or EPA's subsequent testing of fluorinated containers (which results we believe to be inconsistent with the PEER report itself). That said, we plan to continue working cooperatively with EPA to try to narrow down the actual source of these materials.

In addition, Inhance Technologies does not believe that its processes or products are subject to the EPA's PFAS SNUR. As stated in the enclosed response, Inhance Technologies' process does not use or manufacture long-chain perfluoroalkyl carboxylate (LCPFAC). Rather, it uses elemental fluorine to produce fluorinated polymers that are not within EPA's definition of LCPFAC.

Nor does Inhance Technologies' process involve the application of a thin film to articles as a "surface coating" within the meaning of EPA's PFAS SNUR. The SNUR defines a "surface coating" as "a material applied in a thin layer to a surface as a protective, decorative, or functional film." As described in the response, Inhance Technology's process does NOT involve "applyi[ing]" a "thin film" of any PFAS compounds or any compounds for a "functional purpose." On the contrary, as described in the response, even if LCPFAC were produced by Inhance Technologies' processes, they would be formed in very small quantities and serve no purpose for the fluorinated packaging. As such, they would be only "unintentionally present" and therefore exempt from the SNUR pursuant to 40 CFR 721.45(d) as impurities.

Lastly, consistent with our last submittal, please note that since additional submittals from Inhance Technologies will be forthcoming, we have modified the requested IRL Response Statement to reflect this. We will provide a full and final Response Statement at the time that Inhance Technologies has fully addressed each of EPA's requests.

Should you have any questions or concerns about this letter or any of the information provided, please do not hesitate to reach out to me at 407-244-3236 or dwatson@foley.com. I look forward to continuing to work with you on this matter.

Best regards,

Dorothy E. Watson

DEW:

cc: Andrew Thompson

SECOND PARTIAL RESPONSE OF INHANCE TECHNOLOGIES TO EPA TCSA SECTION 11 INFORMATION REQUEST DATED JANUARY 14, 2021

Inhance Technologies LLC ("Inhance Technologies"), hereby submits the following responses and objections to the United States Environmental Protection Agency ("EPA") Request for Information dated January 14, 2021 (the "Information Request"), which EPA issued pursuant to CWA Section 11 of the Toxic Substances Control Act ("TSCA") to investigate "products manufactured, processed or used by [Inhance Technologies] that [EPA determined] potentially contain per and poly fluorinated substances ("PFAS") regulated under [TSCA]. As previously discussed, this first partial response addresses only those requests ("Requests") contained in Section A of the Information Request. Inhance Technologies' responses contained herein ("Responses") are based on its understanding and knowledge as of the date of this response, and Inhance Technologies reserves its rights to supplement and/or amend the Responses, as appropriate. Inhance Technologies further reserves its right to supplement and/or raise any objections it may have to questions not answered in full in this second response.

The Responses are made subject to the General Objections to the Information Request, which are provided in Appendix I and are hereby incorporated into each subsequent Response.

Inhance Technologies Responses to EPA Requests

B. *Process Information.*

1. *Description of the fluorine gas treatment processes used on plastic containers;*

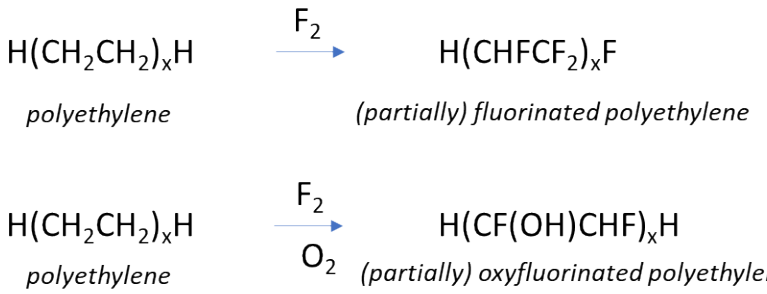
In its Barrier Packaging process, Inhance Technologies modifies certain types of polymers (plastics), using elemental fluorine (F_2). Our use of elemental fluorine to react with plastic containers is intended to impart high-performing barrier properties for packaging of ingredients that would otherwise permeate the container walls. The results of this technological process results in packaging with superior protection against contaminating the environment from unintended releases and against rapid degradation of product efficacy and quality.

There are two types of changes that Inhance Technologies' processes are designed to achieve on polymers. The first relies upon exposure to elemental fluorine to create partially fluorinated polymers. This is the process applied in providing Barrier Packaging services (as described in our prior submittal). The second uses both fluorine and oxygen to create partially oxyfluorinated polymers. This process is more commonly used in the Surface Technologies product line.

As discussed in more detail below, the fluorination process used by Inhance Technologies can be performed on high density polyethylene (HDPE). low density polyethylene (LDPE), or polypropylene (PP).[1] While the exact process depends on the initial

[1] As previously discussed, the material to be fluorinated through either the Barrier Technology or Surface Technolgy product lines is provided by Inhance Technologies' customer.

product to be fluorinated, the basic chemistry is described below for the modification of polyethylene.



The process consists of exposing the containers to fluorine or fluorine and oxygen at pre-determined concentrations under specific environmental conditions. The fluorine gas reacts with the polymers making up the container, to chemically transform them to give them the barrier properties described above. There is no film or "thin layer" of material applied to the containers to achieve fluorination. While polymers on exposed surfaces of the containers are expected to become fluorinated to a greater degree than polymers less exposed to the environment, there are no coatings or layers added to the container or created as part of the container by this process. The modified polymers continue to remain a part of the structure of the container just as they did before the treatment process. Due to the strong bonds forming the polymers, to the best of Inhance Technologies' knowledge and belief, unlike articles that may be coated in a non-polymer perfluorocarbon coating, Inhance Technologies' process does not create any substantial risk of non-polymer PFAS sloughing from the article itself.

Furthermore, the fluorination process is not intended to break the large polymers making up the containers (which have to be composed of at least 100 carbons to be useful for shaping a container) into smaller-chain polymer molecules. The carbon-hydrogen bond is more easily exchanged than the stronger carbon-carbon bond so the primary mechanism is fluorination of the existing polymers. However, even if some production of smaller molecules were possible, it would not be expected to happen to any significant extent during the process given the preferential activity of H-C substitution. However, even if some small amount of shorter length fluorinated carboxylate chemical substances were formed through the fluorination process, their production is neither intentional nor desirable for the product. The value of fluorination comes from the fluorinated polymers themselves. Any perfluorooctanoic acid or LCPFAC (any longchain category of perfluorinated carboxylate chemical substances with per fluorinated carbon chain lengths equal to or greater than seven carbons and less than or equal to 20 carbons) does not contribute to its functionality as barrier packaging, is unintentional and would merely be present as an impurity or byproduct of the process creating fluorination of the plastics polymer itself.

Due to the structure of polymers as well as the inefficiency of the fluorine exposure process associated with this technology, not all hydrogen bonds that are a part of the polymer are replaced with fluorine bonds. For polyethylene, the degree of hydrogen substitution by fluorine is less than 1.6F:1C atom (for reference, the degree of ratio of H:C is 2H:1C for polyethylene). The resulting polymer is not fully (or per) fluorinated. The depth of fluorination generally varies from a few nanometers to a few microns, with a typical depth of

fluorination being up to 3 microns from the surface. However, the actual amount of fluorine substitution achieved and the depth of such substitution is determined by a variety of factors including fluorine concentration, pressure, temperature, and length of exposure.

The chemistry of fluorination of HDPE and other plastics is well-known and has been well studied for decades. Three references are enclosed herewith as Exhibit A to illustrate fluorination in additional detail.

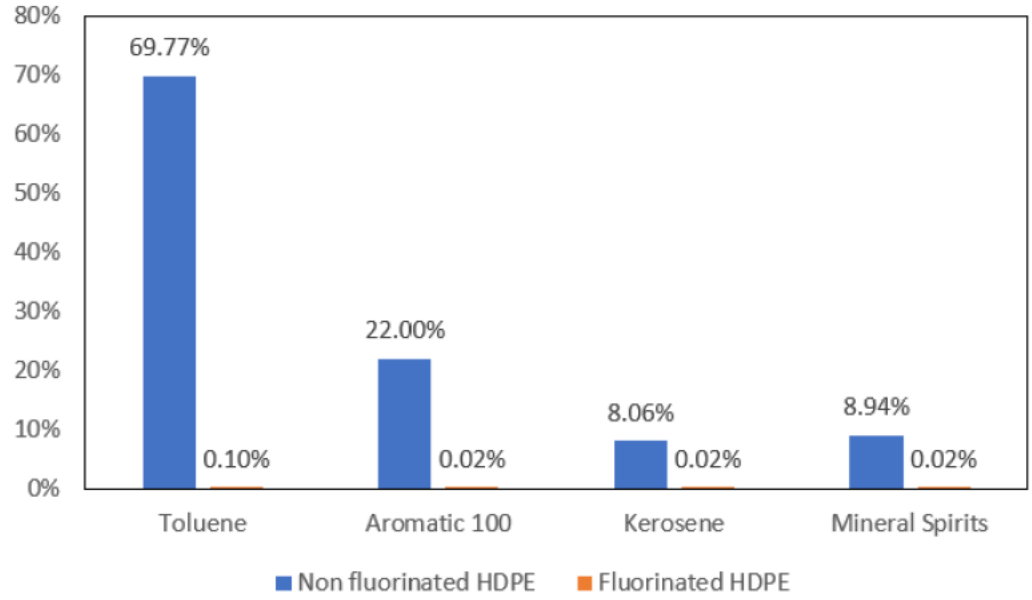
Inhance Technologies barrier technology transforms conventional plastics into high performance barrier packaging. The process creates a permanent barrier that can be applied to polyolefin packaging regardless of shape, size or design. The barrier protects packaging integrity by reducing ingredient loss, increasing shelf life and maintaining product quality. It also helps ensure compliance with packaging regulations, safeguarding health and the environment.

The type of barrier packaging produced by Inhance Technologies is the only fully recyclable (closed loop) barrier packaging technology, and is recognized as such by the (US) Association of Plastics Recyclers (APR) and Plastics Recyclers Europe (PRE). Further, this fluorination technology has the lowest carbon footprint of any barrier packaging technology (as demonstrated by Life Cycle Assessments, LCA, using ISO14044 and ISO14040 standards). See attached Exhibit B. This barrier packaging technology also ensures that products are able to meet US DOT (United States Department of Transportation) regulations including 49CFR178 and 49CFR173. In addition, fluorinated polyethylene has FDA recognition for food contact applications as listed in 21CFR177.1615. In addition, Inhance Technologies also has an active Type III DMF (Drug Master File) registered with the FDA (Drug Master File No. 030719).

This barrier packaging technology creates barrier properties against permeation for a wide range of product ingredients and chemistries. An illustration of the permeation performance of barrier performance is shown below. While untreated polyethylene will allow significant (up to 100% product loss) through container wall permeation, fluorinated polyethylene is very effective in reducing permeation.

Some examples are shown below to illustrate the efficacy of the barrier in preventing solvent permeation and weight loss of ingredients packaged in fluorinated plastic containers. Testing was conducted by filling 32 oz. F-style bottles (non-fluorinated and fluorinated plastic containers) with various solvents, according to DOT 49CFR 173 Part B specifications, at 50°C for 28 days. Bottles were sealed and the cumulative weight loss was measured after 28 days. The % weight loss was calculated and is reported in the chart below. Per DOT specifications, packaging cannot lose more than 2% of its weight during transportation

Content loss through permeation from Fluorinated versus non-Fluorinated HDPE



[redacted]

Inhance Technologies measures the level of fluorination of containers subjected to its process using Fourier Transform Infrared Spectroscopy ("FTIR"). More details on the use of FTIR are provided below. We also periodically measure permeation rates gravimetrically using industry standard test methods as described above.

a. *A spreadsheet, in the format shown below, containing the process variables used to meet customer specifications or to generate the desired container properties. The headings should contain the process variables (i.e. temperature, pressure, time, etc.) and the first column should itemize the product name.*

Inhance offers various levels of fluorination, based on customers' requirements. For barrier packaging, the levels of fluorination provide increasing barrier performance against a wide range of organic permeants. The levels (L1, L2 and so on) of barrier provide environmental protection by keeping the ingredients in

the plastic container, which in turn promotes compliance with relevant DOT regulations, prolongs shelf life and helps maintain product efficacy. The level of fluorination imparted during our process is influenced by temperature, fluorine concentration, pressure, and time of exposure.

In the case of other treatments such as surface technologies, Inhance treats plastic parts using fluorine and oxygen to increase the surface energy ('adhesiveness') of the plastic ("Adhesion" as noted in the below table).

Inhance also treats plastic fuel tanks for permeation compliance with EPA and CARB regulations such as 40CFR1051, 40CFR1060, 40CFR59, TP1501, TP501, and TP901.

Inhance treats polymeric particles and powders ("Ingredients"), using fluorine and oxygen to permanently activate the surface of these particles for enhanced compatibility in coatings, adhesives, sealants and elastomers. These surface-active particles exhibit increased dispersibility in coatings and impart high wear performance characteristics.

Inhance Technologies offers a variety of levels of fluorination across its product lines. [redacted].

Post treatment, fluorinated plastic containers are quality checked using FTIR (Fourier Transform Infrared Spectroscopy) to assure the appropriate level of fluorination. The FTIR technique measures the presence of carbon-fluorine bonds (CF, CF2, and other carbon-fluorine chemical groups) as well as carbon-hydrogen bonds (CH, CH2 and other carbon-hydrogen chemical groups). [redacted] While FTIR techniques are generally only capable of picking up concentrations greater than 1%, this level of sensitivity is more than sufficient for purposes of determining effectiveness of the fluorination process.

Figure A below shows a sample FTIR that comparing an untreated HDPE container (purple) and fluorinated HDPE (red) and can be used to understand how this analysis works. The red line (fluorinated) has a peak that shows the carbon-fluorine bond around 1100 cm-1 wavenumbers (x-axis), while the purple line (untreated) does not show this peak. Instead, the purple line shows three other peaks that are typical carbon-hydrogen peaks at 2900 cm-1, 1450 cm-1 and 750 cm-1.

Figure A

[redacted]

[redacted]

A few representative FTIR spectra for products treated to level 3 and level 5 fluorination are shown in Exhibit C.

b. Explanation of the desired container properties for each product;

Inhance Technologies' barrier technology customers are typically seeking properties including improved barrier against permeation of liquids to be packaged or stored in plastics Inhance Technologies' customers are typically seeking properties including improved barrier against liquids to be packaged or stored in plastics, containers that meet DOT permeability requirements or fuel tanks that are compliant with EPA and CARB regulations. Inhance Technologies works collaboratively with customers seeking the above solutions and provides treatments to meet the customers' needs.

With regards to barrier technologies, customers or potential customers typically send empty sample plastic containers to Inhance Technologies to treat in order for the customer to qualify the fluorinated product as acceptable for the desired use and identify the target level of fluorination for their purposes. T[redacted]

[redacted]. Inhance Technologies does not manufacture or independently procure any of the plastic containers treated, but provides fluorination services on said containers per the customer's specifications.

For quality control purposes, Inhance Technologies routinely verifies that each batch of containers treated meets at least the minimum fluorination level requested by the customer. Occasionally, Inhance Technologies will also verify that permeability remains within acceptable limits. Inhance Technologies does not independently verify other characteristics

As for incoming materials for treatment, Inhance Technologies merely requires that containers to be treated be made of high density polyethylene (HDPE), low density polyethylene (LDPE), or polypropylene (PP). Inhance Technologies staff does a visual inspection of incoming wares to ensure parts are clean, dry, and free of debris prior to accepting them for treatment.

c. *Any standard operating procedures (SOPs) related to the fluorination process;*

Applicable SOPs are provided in Attachment A to the CBI Document

d. *A list of any other process variables used to generate the desired container properties not listed in the spreadsheet B.1.a;*

Other than the process parameters noted above, the process parameters may be modified according to the total surface area including in accordance with the number of articles treated in a batch.

e. *Explanation of the process involved in Level 3 fluorination;*

For level 3 fluorination, the general process is as follows:

[redacted]

[redacted]

f. Explanation of the objective for treatment for each variant of temperature and time (i.e. why is the temperature and time modified?)

The parameters of fluorination are managed to impart the appropriate barrier performance to the plastic container. Time and temperature may be modified to achieve the requested level of fluorination and the barrier level requirement, as specified by the customer. Higher temperatures and longer treatment times promote substitution of C-H with C-F bonds, increasing amounts of which are required to achieve greater levels of fluorination. See Exhibit A for papers addressing the science of direct fluorination.

g. Size of containers treated.

Inhance Technologies has treated plastic containers ranging from less than 2 oz. up to 330 gallons.

2. *Name and composition of the plastic material treated;*

The plastic material used for containers that Inhance Technologies most commonly treats is high density polyethylene (HDPE). Other materials that Inhance Technologies can treat may include LDPE (low density polyethylene) and PP (polypropylene). The articles that Inhance Technologies treats are molded or produced by third parties and provided to Inhance Technologies only for fluorination. Treated containers are directly returned to customers. Inhance Technologies never takes ownership of the containers, nor does it further process or fill the containers. Since Inhance Technologies does not manufacture or procure the containers, the exact composition of containers provided to Inhance Technologies for treatment is not known to Inhance Technologies.

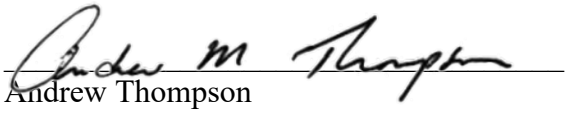
3. *Location of each facility (foreign and domestic) performing the fluorine gas treatment.*

Inhance Technologies incorporates the above general objections and further objects to this question to the extent that it requires Inhance technologies to provide information about facilities that are not under its control or direction. Subject to the general and specific objections, Inhance Technologies replies as follows. Each of the locations identified below is operated by Inhance Technologies LLC, a subsidiary of Inhance Technologies, LLC, or an entity under common control with Inhance Technologies LLC. Facilities identified with as asterisk (*) are Inhance Technologies operations co-located at customer facilities.

Locations	**Which offerings are manufactured at each facility from Question A.2 (scope of business)**
202 Cascade Drive, Allentown, PA 18109	Barrier Packaging, Surface Technologies

29 Royal Drive, Forest Park, GA 30297	Barrier Packaging, Surface Technologies
2800 Industrial Park Road, Centerville, IA 52544*	Barrier Packaging, Surface Technologies
1733 Downs Drive, West Chicago, IL 60185	Barrier Packaging, Surface Technologies
6675 Huntley Road, Suite D, Columbus OH 43229	Barrier Packaging, Surface Technologies
1 Cal Turner Jr Drive, Homerville, GA 31634*	Barrier Packaging, Surface Technologies
22008 N Berwick Drive, Houston, TX 77095	Barrier Packaging, Surface Technologies, Ingredients, Purifying
2226 Commerce Drive, Mt. Pleasant IA 52641	Barrier Packaging, Surface Technologies
6821 Hazelwood Avenue, St Louis MO 63134	Barrier Packaging, Surface Technologies
7211 E 30th Street Suite A, Yuma AZ 85365	Barrier Packaging, Surface Technologies
6814 Kirbyville St, Houston, TX 77033*	Barrier Packaging
279 Pike County Lake Rd, Troy, AL 36079*	Surface Technologies
110B, Delegación Santa Cruz Atzcapotzaltongo, 50030 Toluca de Lerdo, Méx., Mexico	Barrier Packaging, Surface Technologies
Aglomeração Urbana de Jundiaí, Jundiaí - State of São Paulo, Brazil	Barrier Packaging, Surface Technologies
Altebergstraße 27-29, 36341 Lauterbach (Hessen), Germany	Barrier Packaging, Surface Technologies
152 Magowar Rd, Girraween NSW 2145, Australia	Barrier Packaging, Surface Technologies

All statements provided in the above responses to this information request are true and accurate to the best of my knowledge and belief. I acknowledge that this statement is submitted to the United States in connection with a matter within the jurisdiction of the EPA and that any material false statement of fact herein may be a federal crime under 18 U.S.C. § 1001.



Date: 2/8/21

Andrew Thompson
President & CEO
Inhance Technologies LLC

APPENDIX I

Inhance Technologies' General Objections to the Information Request

Inhance Technologies makes the following general objections and hereby incorporates each of them by reference into the Responses set forth below:

1. Inhance Technologies objects to the Information Request and each Request in the Information Request to the extent that it exceeds the scope of EPA's authority to obtain information or documents pursuant to Section 11(c) of TSCA, 15 U.S.C. § 2610(c).

2. Inhance Technologies objects to the Information Request and each Request in the Information Request to the extent that it requests information pertaining to materials not regulated under TSCA.

3. Inhance Technologies objects to each Request in the Information Request to the extent that the Request seeks information or the identification of or production of documents that are not relevant to identifying or assessing products manufactured, processed or used by Inhance Technologies that potentially contain PFAS regulated under TSCA, and are not reasonably calculated to lead to the discovery of material relevant to EPA's implementation of TSCA.

4. Nothing herein shall be construed as an admission by Inhance Technologies regarding the admissibility or relevance of any fact or document. Any production of a document by Inhance Technologies is not a concession or admission that the document or its contents are relevant or complete.

5. Inhance Technologies objects to each Request in the Information Request to the extent that the Request seeks information or the identification or production of documents protected by the attorney-client privilege, the attorney work-product doctrine, or any other applicable privilege.

6. Inhance Technologies objects to each Request in the Information Request to the extent that the Request seeks to impose upon Inhance Technologies an obligation to respond for or on behalf of another party or entity or calls for the disclosure of information or the identification or production of documents not within the possession, custody, or control of Inhance Technologies.

7. Inhance Technologies objects to each Request in the Information Request to the extent that the Request seeks disclosure of information or documents concerning products or services of Inhance Technologies not involving fluorination of plastic containers. Inhance Technologies asserts this objections on the following grounds: (i) such requests are overly broad; (ii) the information and/or documents sought therein is not relevant and not reasonably calculated to lead to the discovery of relevant information; (iii) the information and/or documents sought therein would be unduly burdensome and expensive to disclose; and (iv) the information and/or documents sought therein is potentially privileged and/or of a confidential or proprietary nature, the disclosure of which could adversely affect Inhance Technologies or third parties.

8. Inhance Technologies objects to each Request in the Information Request to the extent that the Request seeks information and/or documents that are confidential, proprietary, or a trade secret, except to the extent such information is protected as Confidential Business Information by requestor. To the extent that Inhance Technologies produces documents or provides information that it considers Confidential Business Information in response to the Information

Request, those documents will be provided in compliance with the requirements of Section 14 of TSCA, 15 U.S.C. § 2613 and 40 C.F.R. § 2.208.

9. Inhance Technologies objects to the definition of the term "PFAS" as vague, ambiguous, overly broad, and unduly burdensome. The present definition of "PFAS" would necessarily include at least 5,000 different chemical substances including but not limited to fluorinated polymers which have been regarded by EPA as substances of low concern. (*See* EPA Polymer Exemption Guidance Manual, Section 4.2.2 (June 1997); *see also* 40 C.F.R. § 721.10536(b)(4)(iii) excluding fluoropolymers as part of articles from the significant new use rule applicable to perfluorooctanoic acid ("PFOA") and its salts).

10. Inhance Technologies objects to the definition of the term "products" as vague, ambiguous, overly broad, and unduly burdensome. Inhance Technologies represents that with the exception of certain polymer ingredients sold to third-parties for further processing, it does not manufacture or import any products. Inhance Technologies does not manufacture or sell plastics or containers. Nor does it manufacture or sell any surface coatings. Therefore, for purposes of the Responses other than Requests 2 and 4, Inhance Technologies clarifies that "products" shall refer to container fluorination services and processes provided by Inhance Technologies associated with their Barrier Packaging business line.

11. Inhance Technologies objects to Request F.1 ("Any other analysis not requested above that Inhance Technology is aware of regarding any treatment involving organic or inorganic fluorine during the last 5 years") as vague and overbroad and therefore unreasonable and unenforceable. See US v. Morton Salt, 338 U.S. 632 (1950).

Exhibit A-1

The kinetics and mechanism of the direct fluorination of polyethylenes

A P Kharitonov,[1] R Taege,[2] G Ferrier[3] and N P Piven[1]

1 Institute of Energy Problems of Chemical Physics (Branch) of the Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432, Russia

2 Air Products GmbH, Fluorine Technology, 45523 Hattingen, Huettenstrasse 50, Germany

3 Air Products PLC, COE Packaged Gases, Weston Road, Crewe, Cheshire, CW1 6BT, United Kingdom

Keywords

Direct fluorination, polyethylene, fluorinated layer, kinetics, mechanism

Summaries

The kinetics and mechanism of the direct fluorination of polyethylenes

Two types of low-density polyethylene (LDPE), five types of high-density polyethylene (HDPE), poly(vinyl fluoride) (PVF) and poly(vinylidene fluoride) (PVDF) were studied. The fluorination of LDPE and HDPE is a diffusion-controlled process and proceeds via a branched chain mechanism following an induction period. Initiation of the reaction takes place via the reaction of molecular fluorine with the C-H bond. The rate of fluorination of HDPE exceeds that of LDPE. PVDF cannot be fluorinated even at temperatures as high as 430K and/or under UV irradiation. The kinetics associated with the formation and termination of peroxy $RO_2^{\bullet}$ and fluorocarbon long-lifetime radicals was studied. It is mainly middle peroxy radicals that are formed at treatment conditions close to those used in industrial processes.

La cinétique et le mécanisme de la fluorisation directe des polyéthylènes

Deux types de polyéthylène de basse densité (LDPE), cinq types de polyéthylène de haute densité (HDPE), le poly(vinyle fluoride) (PVF) et le poly(vinylidène fluoride) (PVDF) ont été étudiés. La fluorisation du LDPE et du HDPE est un procédé à diffusion contrôlée et se déroule au moyen d'un mécanisme à chaîne branchée qui se produit après une période d'induction. L'initiation de l'action se produit au moyen de la réaction du fluor moléculaire avec la liaison C-H. Le taux de la fluorisation des HDPE excède celui des LDPE. Le PVDF ne peut pas être fluoré même à des températures aussi élevées que 430K et/ou sous irradiation UV. On a étudié la cinétique associée à la formation et à la terminaison du peroxy $RO_2^{\bullet}$ et des radicaux fluorocarbone à longue durée de vie. Ce sont pour la plupart des radicaux peroxy centraux qui sont formés sous des conditions de traitement qui sont proches de celles des procédés industriels.

Die Kinetik und Mechanismus der direkten Fluorinierung von Polyethylenen

Zwei Arten von Polyethylen mit niedriger Dichte (LDPE), fünf Arten mit hoher Dichte (HDPE), sowie Polyvinyl-Fluorid (PVF) und Polyvinylidene-Fluorid (PVDF) wurden untersucht. Die Fluorinierung von LDPE und HDPE ist ein diffusionskontrollierter Prozeß, der durch eine verzweigte Kettenreaktion nach einer Induktionsperiode abläuft. Der Prozeß wird durch die Reaktion von molekularem Fluorin mit der C-H Verbindung in Gang gesetzt. Die Fluorinierungsrate von HDPE ist größer, als die von LDPE. PVDF kann selbst bei hohen Temperaturen (430 °K) und/oder UV-Licht nicht fluoriniert werden. Wir erforschten auch die Kinetik der Formation und Terminierung von Peroxy $RO_2^{\bullet}$ und die langlebigen Fluorkarbonradikale. Unter den in Industrieprozessen üblichen Operationsbedingungen werden vor Allem die mittleren Peroxyradikale gebildet.

For correspondence contact

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Introduction

Surface modification is a well-established method for enhancing the performance of polymeric materials in a number of applications,[1] and one of the more effective methods of surface modification is direct fluorination (ie the treatment of a polymer surface with gaseous fluorine or a fluorine-containing mixture). Due to relatively weak F-F bonds and strong C-F bonds, fluorination can proceed at a rate acceptable for industrial processes at ambient temperatures without the need for any initiation process.[1,3] An important practical application of direct fluorination is the enhancement of the barrier properties of industrial polymer components. As an example, the fluorination of plastic gasoline automobile tanks can result in an approximately one hundred-fold decrease in the loss of fuel from a tank when compared with that from virgin, untreated tanks.[1,4] Such an enhancement enables compliance with legislation relevant to the permeation of volatile organic compounds from automobile fuel tanks into the general environment. It is worth noting that under industrial conditions, a surface layer of only around 0.1 to 10μm in thickness is modified during the fluorination process and the bulk of the polymer remains unchanged.

The majority of research in this field has until recently been mainly concerned with the practical applications of direct fluorination and only a limited number of investigators have focused upon the fundamental aspects of the direct fluorination of polyethylene. In addition, there seems to be a number of discrepancies between the various findings as reported in the literature.

According to some authors, the fluorination of polyethylene (PE) results in the total replacement of hydrogen atoms with fluorine to form a PTFE (polytetrafluroethylene)-like structure $(–CF_2–CF_2-)_n$.[5,6] However, such a modification requires a considerable amount of time (ie from several weeks to several months). An almost complete degree of substitution of H- with F-atoms was reported by Hara, Fukumoto and Watanabe[7] for HDPE films (UltZex2021L from Mitsui ekiyu Kagaku Kogyo) which had been subjected to a treatment time of 15 hours at 0.2 bar F_2 pressure with a temperature of 100°C; conditions which are distant from those in an industrial environment. Other authors have found that the fluorination of PE within a commercially acceptable timescale (ie of around one hour) did not result in the total replacement of the H-atoms (ie the maximum possible ratio of F/C = 2 was never attained). Examples of this include work by Corbin *et al* who found that surface fluorination led to a surface F/C ratio of only 0.84 following treatment with a 5%F_2/95%Ar mixture for one hour at room temperature.[8] Similarly, a range of F/C ratios have been reported, following treatment with a variety of mixtures, including 1.69,[5] 1.33,[9] and 1.5.[10] Similarly, the fluorination of PVF as reported by Corbin *et al*[8] did not result in the total substitution of H-atoms for F-atoms but only led to the formation of a polymer on the surface with a F/C ratio of 0.70 after treatment with a 5% F_2/95% Ar mixture at STP (standard temperature and pressure) for one hour.[8] Shinohara *et al*[11] noted a F/C ratio of only 1.25 after treatment with 300 to 800 Torr of fluorine at room temperature, although the F_2 used in these studies contained around 1.6% of oxygen.

No change of surface chemical composition was found following fluorination of PVDF[8] and no mass change was detected upon fluorination of PVDF *in situ*.[12] However, on the contrary, according to Scherer *et al*,[13] the chemical composition of PVDF may be changed through fluorination to give a F/C ratio of 1.9.

The presence of oxygen in a fluorinating mixture, either through controlled addition or as an intrinsic contaminant, results in the formation of carboxylic acid –C(O)F groups which are themselves transformed into carbonyl –C(O)OH groups upon contact with water vapour. The concentration of –C(O)F groups in LDPE[2] can reach $1.8{\cdot}10^{-2}$mole•g^{-1}.

The kinetics of formation of fluorinated layers has been studied by a number of investigators, although no measurements were carried out *in situ* (ie during the fluorination process). All measurements were carried out in such a manner that fluorination was halted, and the sample then removed from the reaction vessel following which the measurements were carried out. Attenuated total reflectance spectroscopy has been used to measure the thickness δ_F of fluorinated layers of HDPE.[14] The authors proposed a linear dependence between δ_F and the time of fluorination t but when the results were converted by the authors of this paper into a $log(\delta_F)$-$log(t)$ scale, the following relationship was obtained: $\delta_F \sim t^{0.70}$. The fluorinated layer of a sample of PE was separated from untreated polymer by boiling in xylene[10] and the experimentally determined dependence between δ_F and t was close to $\delta_F \sim (p_F{\cdot}t)^{0.5}$, where p_F is the fluorine partial pressure. A quartz crystal microbalance technique was used to measure the dependence of the mass of HDPE films on the treatment time *in situ*.[7] A mixture of 5 to 20% of F_2 in Ar was used to carry out fluorination over a temperature range between 27 and 100°C. During the initial stages (ie the first few minutes), the rate of fluorination was very slow, but subsequently the increase in the mass of the film became proportional to the square root of the fluorination time when the fluorine partial pressure and temperature were held constant. Unfortunately, the calculations of the activation energy associated with the rate of fluorination were not correct as the authors took into account only fluorine diffusion and not fluorine consumption during the course of the chemical reactions. The change of polymer film weight during fluorination was monitored *in situ*.[12] LDPE (density 0.921g cm^{-3} from Plastomark), HDPE (density 0.950g cm^{-3} from AECI), PVF, PVDF, polypropylene (PP, density 0.907g cm^{-3} from Sasol Polymers), and a copolymer of PE and PP (PP-co-PE, density 0.900g cm^{-3} from Sasol Polymers) were used. Mixtures containing 5 and 10% of F_2 and He, N_2, O_2 and CO_2 at ambient pressures were used for treatment over a range between 28 and 70°C. Again it was found[7] that during the initial stages (ie within one to two minutes) the rate of fluorination was very slow, but subsequently the increase in mass became proportional to the square root of the time of fluorination. The increase of the concentration of fluorine in a fluorination mixture and elevation of treatment temperature resulted in a significant increase in the rate of fluorination. The replacement of N_2 with He resulted in a slight decrease of the fluorination rate but O_2 strongly inhibited the reaction. No reaction was detected between F_2 and PVDF at 50°C for one hour. The rate of fluorination was noted to increase in the order LDPE < PVF < HDPE < (PP-co-PE) < PP. Nazarov *et al*[15] studied the dependence of the mass increase for HDPE, LDPE and PP on the time of fluorination and showed that the rate of fluorination increased with fluorine concentration and in the order HDPE < LDPEPP. Oxygen was found to strongly inhibit the reaction with an increase in oxygen concentration in the fluorinating mixture from 0.1 to 1 volume percentage resulting in an almost ten-fold decrease in the fluorination rate.

It was noted that long-lifetime peroxy RO_2, and possibly perfluoroalkyl radicals, are formed as end-point products

of the direct fluorination of PE.[16–18] The concentration of peroxy radicals was estimated,[16] in the case of PE, as between (2…3) 10,[18] and (2…5) 10^{17} radicals.g^{-1}.[18] However, it should be emphasised that the experiments were carried out with thick PE samples which were not fluorinated to their full thickness. The radical concentration was then estimated over the complete sample, not distinguishing between its fluorinated surface layer and its non-fluorinated part. The lifetime of the radicals in fluorinated polymers was not reported.

On the basis of the above literature review, the following summary can be made. There seems to be no direct experimental confirmation of the existence of a sharp thin boundary transition zone between fluorinated and untreated PE layers and no evidence that the direct fluorination of PE occurs as a diffusion-controlled reaction. In addition, the relationship between the thickness of a fluorinated layer and the time of fluorination has not been determined *in situ*. Only the gross chemical compositions (ie the ratios of F/C/O/N) have been studied and minor chemical compositional changes ignored. Neither the actual concentration of long-life radicals inside a fluorinated layer nor their termination kinetics have been measured. Transient species, such as radicals of a relatively short lifetime which take part in the chain continuation processes, have not been monitored or identified, and a scheme to describe the elementary stages of a fluorination process has only been proposed and not verified through experimentation.

This paper will provide further insight into the details of the reaction of polyethylene and fluorine, with reference to the research described in earlier publications.[19–21]

Materials

The fluorine used in the work reported here contained less than 0.1 volume percent of oxygen. For a particular set of experiments, the additional purification of fluorine was carried out using the method of Shamir and Binenboym.[22] A mixture of F_2 and SbF_5 was irradiated inside a stainless steel vessel by ultraviolet (UV) light from a mercury lamp for one hour through a sapphire optical window. Residual O_2 was removed by the reaction of F_2, O_2 and SbF_5 to form solid O_2SbF_6. Nitrogen and helium used in this work were of 99.995% purity. Two types of LDPE (densities 0.926g cm^{-3} and 0.918g cm^{-3} from Aldrich), five types of HDPE marked by figures no 1 – BP (density 0.947g cm^{-3}, melt index ((190C/21.6): 6.1g/10 minutes, colourless), no 2 – Elenac (density 0.945g cm^{-3}, melt index (190C/21.6): 6g/10 minutes, colourless), no 3 – Atofina (density 0.949g cm^{-3}, high load melt index: 8.0g/10 minutes, black), no 4 – Borealis (density 0.948g cm^{-3}, melt index (190C/21.6): 7.0g/10 minutes, colourless/UV stabilised), no 5 – Solvay (density 0.946g cm^{-3}, high load melt index: 4.2g/10 minutes, contains 0.2% of carbon black), PVF (poly(vinyl fluoride) (Scientific Polymer Products Inc, Ontario, Canada), and PVDF (poly(vinylidene fluoride) (Fluorochem Limited, Derbyshire, UK) were used. A set of flat films with a very smooth and reflective surface was prepared with a hot press. In some experiments, LDPE was used in the form of a cotton wool. This was fabricated by dropping a solution of LDPE in hot o-xylene into ethanol. The precipitate was then allowed to dry at an elevated temperature.

Experimental

An original kinetic interference method using visible light was used to investigate the relationship between the resulting thickness of a fluorinated layer δ_F and the duration of the fluorination process.[23–30] Very flat films of high reflectance were used and the intensity I of a light (at a fixed wavelength λ=0.6328μm) reflected at a 45° angle from the surface of the polymer film (which had been treated in the reaction vessel by fluorine) was monitored. If the untreated and fluorinated polymer layers are separated by a very thin transition (boundary) layer parallel to the upper polymer surface (see Figure 2: thickness of this boundary layer must be much smaller than $\lambda/4$) (ie the fluorinated layer thickness was uniform across the polymer surface), the intensity I of light (at a fixed wavelength λ) has interference features (ie the intensity of light depends on time and consists of a series of maxima and minima – see Figure 3 in reference 28). These interference features are due to the interference of two light beams: (a) reflected from the fluorinated film surface- gaseous phase boundary; and (b) reflected from the fluorinated film-untreated film boundary. The first minimum corresponds to the thickness of the anti-reflecting layer (fluorinated layer thickness $\delta_F = b\cdot(1/4)\cdot\lambda/n_F$ where n_F is the refractive index of the fluorinated polymer, coefficient $b = [1-(\sin\beta)^2(n_F)^{-2}]^{0.5}$ takes into account the refraction of the beam falling at the angle β on the surface of a polymer films (in the authors' experiments $\beta = 45°$), the first maximum corresponds to $\delta_F = b\cdot(1/2)\cdot\lambda/n_F$ and so on.[27]

This method allows the measurement of the thickness of the fluorinated layer from $\delta_F \sim 0.13\mu$m for $\lambda = 0.6328\mu$m (a He-Ne laser was used as a light source; the upper limit of the δ_F value depends on the type of polymer under study; for example, in the case of polystyrene it exceeded 50μm).[28] The main advantage of this method is that it is non-destructive and the relationship between the thickness δ_F of the fluorinated layer with time can be monitored in situ (ie the fluorination procedure is not interrupted by the measurement process). A Spekord UV-VIS (Karl Zeiss Jena) spectrometer was used to measure spectra in the visible region. Visible spectra have equidistant (in wavenumber scale) interference features and these spectra were used to calculate the thickness of the fluorinated layer of the fluorinated films. To measure spectra in the infrared (IR) region, a FTIR spectrometer FT-02 (Lumex, Russia) was used. At least 100 scans (usually at 4cm^{-1} resolution) were collected to obtain a single IR spectrum. A special reaction vessel equipped with ZnSe optical windows (stable to fluorine action and transparent over ~20,000 to 500cm^{-1}) was developed and fabricated. This reaction vessel allowed measurement of the spectra of fluorinated films in a vacuum (ie to minimise the influence of atmospheric moisture). An electron spin resonance (ESR) spectrometer SE/X 2544 (Radiopan) was used to monitor ESR spectra and this was connected directly to a sampling system to allow for the direct introduction of fluorine into the reaction vessel located within the ESR resonator, and again enable the study of the kinetics of fluorination *in situ*. ESR spectra could be measured over a 77 to 295K temperature interval. VLR-200 balances were used to measure weight with an accuracy of 0.5mg, and a repeatability of 0.05mg.

Results and Discussion

Kinetics of formation of a fluorinated layer

The visible spectra (0.4 to 0.7μm) of fluorine-treated PE films (HDPE and LDPE) have a distinct interference structure (see Figure 1). These spectra can be explained using a multilayer model of a fluorinated polymer film, as previously reported.[28,30] If the film is treated simultaneously on both sides, the fluorinated film consists of (1) a fluorinated layer, (2) a boundary transition layer, and (3) a virgin, untreated layer (see Figure 2). Interference features can arise only in the case when the thickness δ_b of a boundary transition layer is much less than

$\lambda/(4 \cdot n_F)$, where λ is the wavelength of visible light and n_F (for the majority of fluorinated polymers n_F ~1.35 to 1.45) is the refraction index of the fluorinated layer in the visible region of the spectrum. Hence, it can be estimated that $\delta_b \leq 0.07$mm and that direct fluorination can be considered a surface phenomenon (ie the reaction proceeds as a diffusion-limiting process). The majority of the chemical reactions occur inside this transition boundary layer and the majority of the physical and chemical properties such as density, refraction index, chemical composition etc of the polymer are mainly only changed within this layer. The rate of formation of the fluorinated layer is limited by the permeation rate of fluorine from the gaseous phase penetrating through the fluorinated layer into the virgin layer. In this case the kinetic interference method previously described can be applied.

The dependence of the thickness δ_F of a fluorinated layer on the time of fluorination t in the case of LDPE (density 0.926g cm^{-3}) is shown in Figure 3. The data points ($\delta_F = 0$, $t = 0$) are ignored in order to facilitate linear regression. Similar dependences were obtained in the treatment of LDPE (density 0.926g cm^{-3}) with 9.7% F_2 + 90.3% He mixture and in the treatment of LDPE (density 0.918g cm^{-3}) with undiluted fluorine. When a fluorinated layer of a thickness of ~0.1μm is formed, the dF value depends on the square root of the time of fluorination t:

$$\delta_F = A \cdot t^{0.5} + b \qquad \text{Equation 1}$$

The following quantitative expressions can be obtained from the experimental data (p_F- in bars, t- in seconds):

LDPE, density 0.926g cm^{-3}, treatment with undiluted fluorine:

$$\delta_F = 4.27 \cdot 10^{-4} \cdot p_F^{0.56} \cdot t^{0.5}$$

LDPE, density 0.926g cm^{-3}, treatment with 9.7% F_2 + 90.3% He mixture:

$$\delta_F = 4.07 \cdot 10^{-4} \cdot p_F^{0.57} \cdot t^{0.5}$$

LDPE, density 0.918g cm^{-3}, treatment with undiluted fluorine:

$$\delta_F = 6.46 \cdot 10^{-4} \cdot p_F^{0.52} \cdot t^{0.5}$$

The dependence of factor A on the fluorine partial pressure p_F for the two types of LDPE and for various fluorinating mixtures (undiluted fluorine and 9.7% F_2 + 90.3% He) are shown in Figure 4. The experimental results lead to the conclusion that even a tenfold dilution of fluorine with an inert gas does not significantly influence the rate of formation of a fluorinated layer on either heavier LDPE types (0.926g cm^{-3}) or on the less dense LDPE types (0.918g cm^{-3}). The experiments prove, however, that the rate of fluorination is proportional to the density of the chosen LDPE under examination. In this context it should be noted that none of the linear regressions obtained from the results of actual experiments crossed the origin of the coordinate system ($\delta_F = 0$, $t = 0$) but intersected the t-axis at t = (1–3) minutes. Similar results have been reported elsewhere.[7,12]

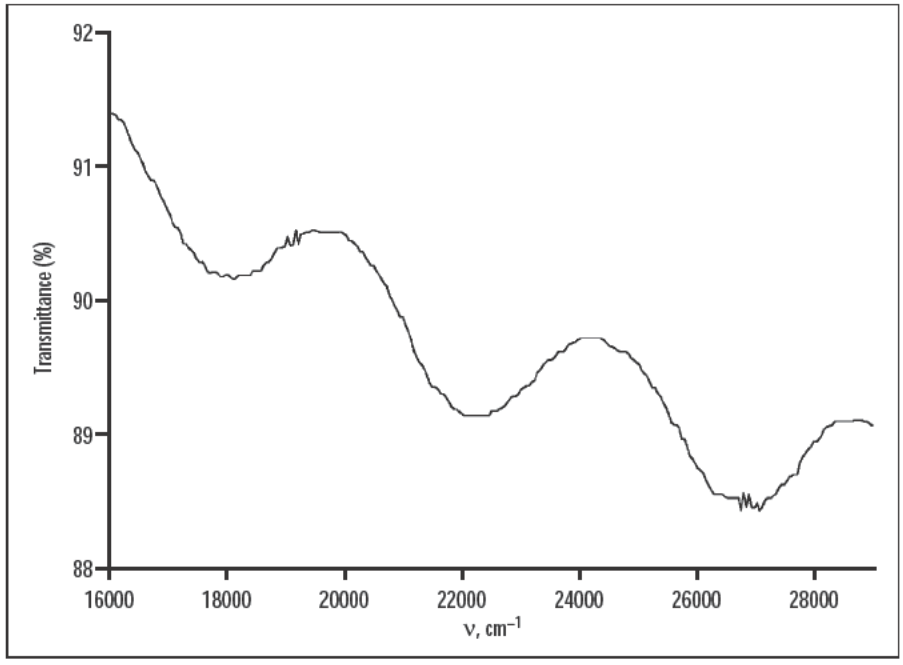

Figure 1: Transmittance of fluorinated LDPE flat film versus wavenumber ν

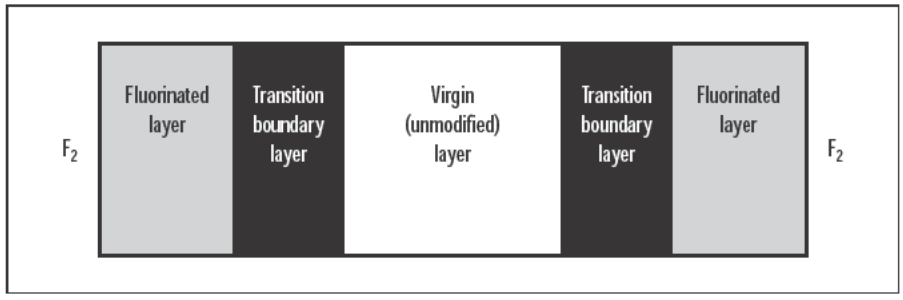

Figure 2: Cross-cut of a polymer film treated with fluorine

The dependence of the thickness δ_F of a fluorinated layer on the fluorination time t for the HDPE sample nos 1 to 5 is shown in Figure 5 along with the results obtained with the LDPE (0.926g cm^{-3}), LDPE (0.918g cm^{-3}) and PVF. In either case, the data points ($\delta_F = 0$, $t = 0$) were ignored in order to facilitate linear regression.

In contrast, all the attempts to effect the fluorination of PVDF were unsuccessful. PVDF was treated (a) with a 20% F_2/80% He mixture (total mixture pressure 1 bar) at T = 293K for four hours; (b) with a 20% F_2/80% He mixture (total mixture pressure 1 bar) at ~420K for four hours; and (c) with a 20% F_2/80% He mixture (total mixture pressure 1 bar) at 293K for ten hours under UV irradiation from a mercury discharge lamp (electric power 250W). The experiments did not result in any change in the IR spectra of the relevant polymer samples nor in any change in the sample weights. The experiments prove that PVDF resists fluorination even under rather extreme reaction conditions.

The influence of the treatment temperature on the rate of formation of fluorinated surface layers on polyethylene was studied in experiments with fluorine-nitrogen blends with 10% fluorine concentration (see Figures 6 and 7). While the total gas pressure in all experiments was 1 bar.a, treatment temperatures between 297.7 and 341.2K (24.5 to 68°C) were applied. The treatment time t was between ~3 and 5 hours. As mentioned above, diluting the fluorine with inert gas had virtually no effect upon the rate of the fluorination reaction. Also, nitrogen only slightly affected the reaction rate of surface fluorination. In addition, a typical induction period was observed which lasted until the flu-

orinated surface layer had reached a thickness of δ_F ~0.13μm. Beyond that, surface layer formation proceeded with the square root of the treatment time, according to Equation 1.

The dependence of the pre-exponential coefficient A (μm.s-0.5, see Equation 1) on the treatment temperature T (K) is shown in Figure 5 and can be described as follows:

$$A = 0.59 \cdot 10^{-(597/T)} \qquad \text{Equation 2}$$

Kinetics of formation of fluorinated layer – Summary

(a) The fluorination of polyethylene proceeds via a branched chain mechanism following an induction period.
(b) The fluorination of LDPE and HDPE is a diffusion-controlled process. This indicates that the rate of formation of a fluorinated layer is limited by the rate of penetration of fluorine through the fluorinated polymer layer into the untreated layer. The fluorinated and untreated layers are separated by a very thin transient boundary layer where the majority of the chemical reaction takes place.
(c) The rate of formation of a fluorinated layer increases with fluorine partial pressure and temperature and was not observed to be affected by the presence of He and/or N_2 in the fluorinating mixture.
(d) There is practically no correlation in the rate of formation of the fluorinated layer with the actual density of the HDPE or with the presence of additives such as carbon black.
(e) The rate of fluorination of HDPE significantly exceeds that of LDPE.
(f) PVDF cannot be fluorinated even at temperatures as high as 430K and/or under UV irradiation.
(g) The fluorination rate of PVF is almost identical to the fluorination rate of LDPE.

The relationship between fluorination and chemical composition: IR study

Two types of LDPE with a density of 0.926 and 0.918g cm^{-3} were studied by IR spectroscopy. Band assignments were made on the basis of Socrates.[31]

LDPE with density 0.926g cm^{-3}

Figure 8 shows (1) the spectra of virgin LDPE; (2) the spectra of surface-fluorinated LDPE (δ_F = 0.39μm) treated at room temperature with undiluted fluorine at a fluorine partial pressure of p_F = 147 Torr , for t = 85 minutes; and (3) the spectra of surface-fluorinated LDPE (δ_F = 0.75μm) treated for t = 16 hours, at room temperature and 1 bar total gas pressure with a three-component mixture consisting of 2.8% fluorine, 9.4% oxygen and 87.8% helium, at a total pressure of 1 bar (p_F = 70 Torr). It is pertinent to note that the spectra shown in Figure 8 were measured repeatedly for several hours following fluorination (ie during this period all the samples were in contact with atmospheric air for several hours and were thus subjected to hydrolysis).

The action of fluorine substantially changes the IR spectra of the virgin LDPE films. Moreover, it was clear from the changes in the IR spectra that reactive components present in the fluorinating mixture influenced the chemical composition of a fluorinated surface layer. The main feature in the IR spectra of LDPE treated with undiluted fluorine is a very broad diffuse band over the 1000 to 1300cm^{-1} region. Two maxima within that band located at 1183 and 1148 cm^{-3} are due to the absorption of C–F, FCF and F_2CF bonds. This means that a substantial quantity of partially fluorinated groups (eg –CHF–) are present in a fluorinated polymer. The intensity of the diffuse band increases with the thickness of the fluorinated layer. The spectrum of LDPE treated with an oxygen-containing F_2/He mixture substantially differs from

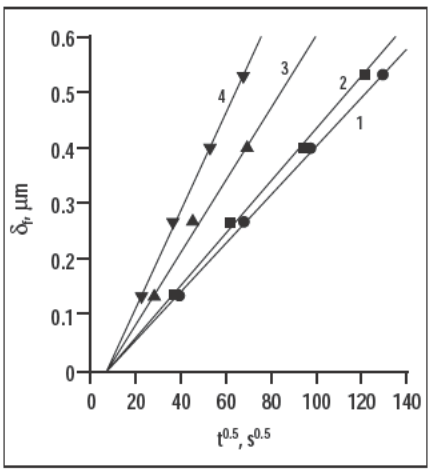

Figure 3: Dependence of the thickness δ_F (µm) of a fluorinated layer on fluorination time t (s) in the case of LDPE with a density of 0.926g cm^{-3}. All treatments were with undiluted fluorine and curves 1 to 4 correspond to the fluorine pressures of 58.8, 88.2, 147 and 205.8 Torr, respectively. Treatment temperature: 293.5 ± 0.5K. Data points at (δ_F = 0, t = 0) were ignored to facilitate linear regression

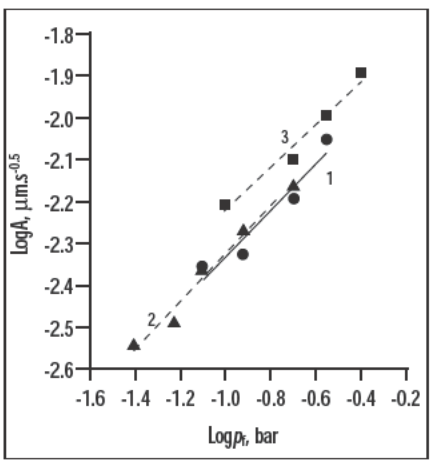

Figure 4: The dependence of the value of A (µm.s$^{-0.5}$) (see Equation 1) on fluorine partial pressure p_F (Torr). 1: – LDPE density 0.926g cm^{-3}, treatment with undiluted fluorine; 2: triangles – LDPE density 0.926g cm^{-3}, treatment with mixture 9.7% F2/90.3% He; 3: squares – LDPE density 0.918g cm^{-3}, treatment with undiluted fluorine

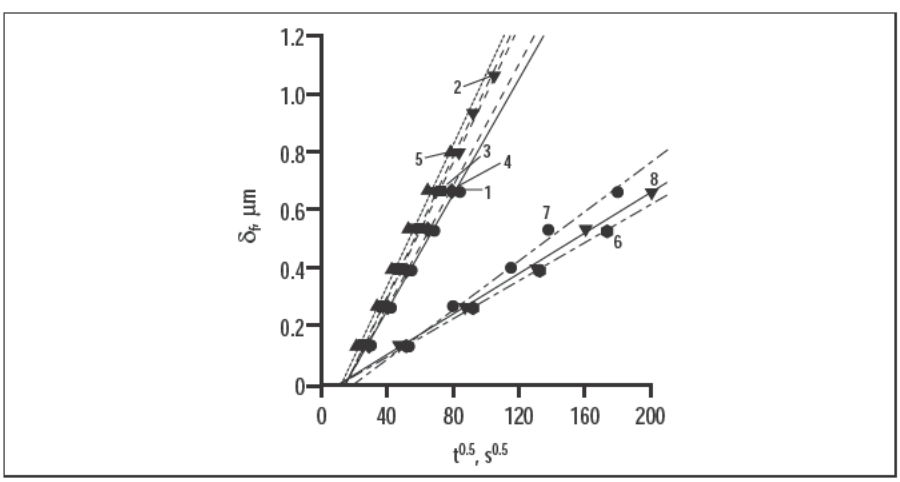

Figure 5: The dependence of the thickness δ_F (µm) of a fluorinated layer on the time of fluorination t (s). Treatment with undiluted fluorine at p_F = 35.3 Torr. 1 to 5: HDPE marked by numbers 1 to 5 correspondingly; 6: LDPE density 0.926g cm^{-3}; 7: LDPE density 0.918g cm^{-3}; 8: PVF. Treatment temperature: 293 ± 1K. Data points at (δ_F = 0, t = 0) were ignored to facilitate linear regression

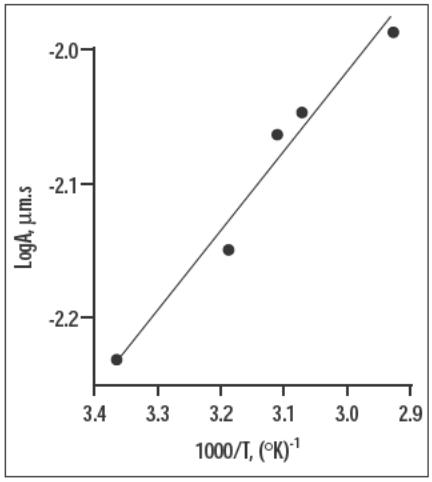

Figure 7: Dependence of the pre-exponential factor A (µm.s$^{-0.5}$) (see Equation 1) on the reciprocal of treatment temperature T (semi logarithmic scale) for the data shown in Figure 6

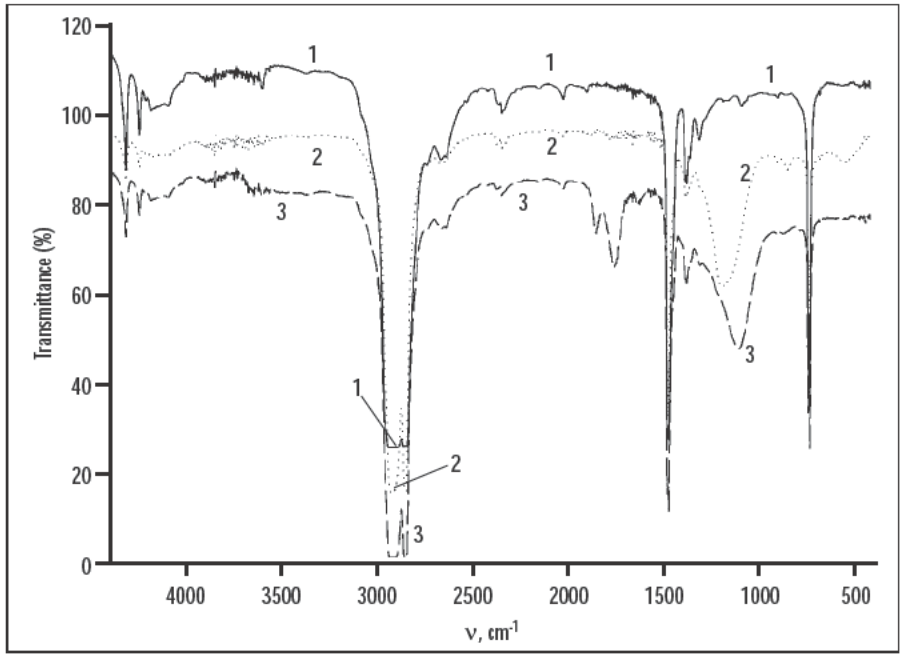

Figure 8: IR spectra of virgin and treated LDPE (density 0.926g cm^{-3}). 1: virgin LDPE; 2: LDPE treated with undiluted F2 (p_F = 147 Torr, treatment time t = 85 minutes at T = 293K, thickness of fluorinated layer δ_F = 0.39µm); 3: LDPE treated with a O_2/F_2/He = 2.8/9.4/87.8% mixture. Total pressure 1 bar, p_F = 70.2 Torr, t = 16 hours at T = 293K, δ_F = 0.75mm. Curves were shifted along the Y axis to prevent overlapping

the spectrum of LDPE treated with undiluted, pure fluorine. At first the absorption maximum of the previously mentioned diffuse band system shifts to 1093cm^{-1}. The shift can be associated with the preferred formation of monofluorinated compounds such as –CHF– and –C (O)F–. The formation of C=O bonds is evident from the appearance of the bands between 1600 to 1900cm^{-1}. A more detailed discussion on those bands will be presented.

An unsupported film of LDPE (density 0.926g cm^{-3}) was treated with an oxygen-containing fluorine blend in the ratio O_2/F_2/He = 1%/10%/89% at a total pressure of 1 bar.a and T = 293K. The IR spectra of the untreated, virgin and treated samples are shown in Figure 9. The band over the range 2290 to 2375cm^{-1} can be ignored due to the IR absorption by CO_2 in the gas phase. Diffuse bands over ~1000 to 1400cm^{-1} corresponded to various C-F absorptions. To separate overlapping bands, computer simulation was applied. It was clearly evident that in freshly fluorinated samples (ie treated with mixtures of F_2/O_2), four bands at 1853, 1762, 1741 and 1622cm^{-1} arose.

The absorption at 185cm^{-1} can be attributed to a carbonyl vibration in a –C(O)F group. The band at 1762cm^{-1}-can be assigned to the C=O vibration in the α-fluoro-ketone –CHF–(C=O)–CHF- while the band at 1741cm^{-1} can be attributed to the C=O vibration in the α-fluoroester –CHF–C(=O)–O– or the α-fluoro-ketone –CH_2–(C=O)–CHF–.

A weak band at 1622cm^{-1} can be attributed to both C=O vibration in the enol form of the β-diketones –C(=O)–CF=C(OH)– or the double bond C=C (eg –FC = CH–) stretching vibration.

After hydrolysis (see curve 3), three new absorptions at 1736, 1653 and 1623cm^{-1} arose; to separate the bands, the above-mentioned computer simulation was applied, while the band at 1853cm^{-1} disappeared as result of the acid fluoride hydrolysis: –COF + H_2O ⇒ COOH + HF.

The 1736cm^{-1} band was probably the C=O vibration in either –CHF–C(=O)OH– or the α-fluoroester –CHF–C(=O)–O– or the α-fluoroaldehyde –CHF–C(=O)H or the α-fluoro-ketone –CH_2–(C=O)–CHF–.

Newly formed C=C bonds were most likely responsible for the absorption at 1653cm^{-1}. The band at 1623cm^{-1} can be assigned to both the C=O vibration of the enol form of the β-diketones –C(=O)–CF=C(OH)– and to the double bond C=C (eg –FC=CH–) stretching vibration.

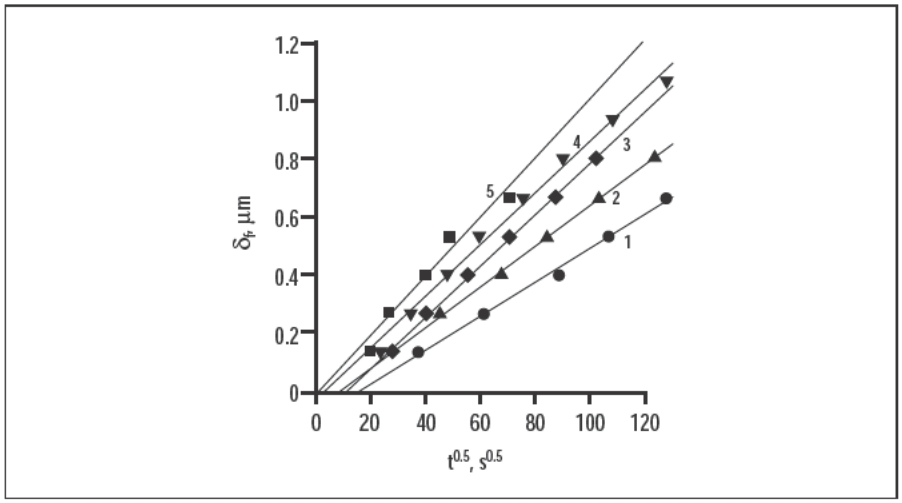

Figure 6: Dependence of the thickness δ_F (µm) of a fluorinated layer on fluorination time t (s). LDPE density 0.918g cm^{-3}. Fluorinating mixture: 10% F_2/90% N_2. Total mixture pressure was equal to 1 bar. Treatment temperature T was equal to 297.7, 313.2, 321.7, 325.7 and 341.2K (24.5, 40.5, 48.5, 52.5 and 68°C) for curves 1 to 5 respectively. Data points at δ_F = 0, t = 0 were ignored to facilitate linear regression

LDPE with density 0.918g cm^{-3}

The IR spectra and chemical composition of fluorinated LDPE with a density of 0.918g cm^{-3} were very similar to that

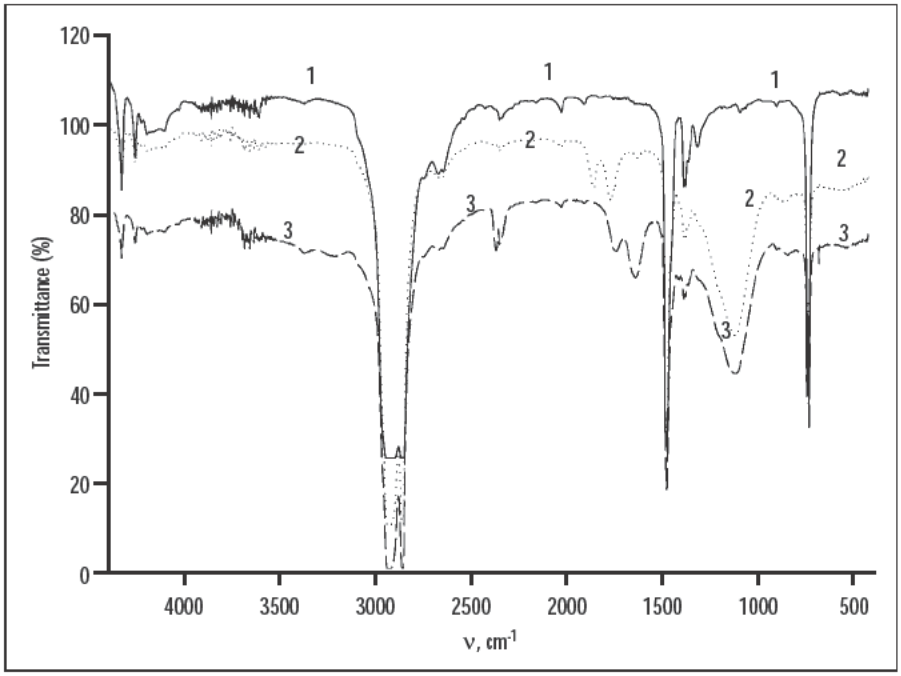

Figure 9: IR spectra of virgin and treated LDPE (density 0.926g cm^{-3}). 1: virgin LDPE; 2: LDPE treated with an O_2:F_2:He mixture of a ratio of 1:9.7:89.3 (total pressure 1 bar, pF = 70.2 Torr, t = 16 hours at T=293K, δ_F = 0.81μm), spectrum measured three minutes after removal of the film from the reactor; 3: the same film following two months of storage in ambient air. The curves were shifted along the Y axis to minimise overlapping

Table 1: Concentration $N_{C=O}$ of carbonyl groups in LDPE treated under different conditions. Films were treated on both sides so that a double thickness of fluorinated layer was used in the calculations. The fluorine contained ~0.1 volume percent of oxygen as contaminant

LDPE density (g cm^{-3})	*Fluorination mixture*	*Mixture pressure (bar)*	$N_{C=O}$
0.926	O_2:F_2:He = 1:10:89	1	0.49
0.926	O_2:F_2:He = 2.8:10:87.2	1	0.48
0.918	O_2:F_2:He = 0.4:10:89.6	1	0.27
0.918	O_2:F_2:He = 2:10:88	1	0.73
0.918	F_2	0.2	0.04–0.06

in the case of LDPE with a density of 0.926g cm^{-3}. Therefore, the results on LDPE with a density of 0.918g cm^{-3} are not discussed in this paper. Details can be found in the authors' recent publication.[21]

There are two possible explanations for the formation of the C=O groups:

1. the oxyfluorination of $-CH_3$ groups (ie reaction between $-CH_3$ groups, O_2 and F_2); or
2. scissions of the main polymer chain.

To evaluate the amount $N_{C=O}$ of C=O-containing groups per monomer unit, the method described in reference 28 was applied and the results of $N_{C=O}$ measurements are shown in the Table 1. Even a small concentration of oxygen in the fluorinating mixtures can promote the formation of C=O containing groups in LDPE significantly. A similar argument was provided by Lagow *et al*.[2]

To evaluate the concentration of $-CH_3$ groups in LDPE (density 0.918g cm^{-3}), the IR method described in reference 32 was applied. The measured amount of $-CH_3$ groups per 1000 carbon atoms was equal to 24.2. It was evident that even 0.4% of the oxygen in a fluorinating mixture would result in a chain scission because the concentration of $-CH_3$ groups was far too low to explain the amount of C=O groups which were formed. It is therefore self-evident to conclude from the results discussed above that the presence of oxygen during surface fluorination can have a significant effect via chain scission upon the final attributes of a fluorinated surface layer such as its barrier properties. Moreover, with regard to the surface fluorination of polyethylene, it can be concluded that the presence of oxygen in a fluorinating gas mixture has a strongly negative influence upon the resulting barrier properties of surface-treated substrate material.

The relationship between fluorination and chemical composition – IR study – Summary

(a) Fluorination results in a replacement of hydrogen atoms by fluorine atoms, but the fluorination inside the fluorinated layer is not complete. Also a set of minor groups may be formed. The presence of oxygen (even in trace amounts, ~0.1 volume %) results in the formation of C=O-containing groups which can be hydrolysed through the activity of moisture. Those groups are hydrolysed through the action of moisture into –COOH groups.

(b) The presence of oxygen contaminants at levels as low as 0.5% results in the formation of remarkable amounts of =O-containing groups and leads to chain scission.

The kinetics of formation of long-life radicals

A LDPE with a density of 0.918g cm^{-3} was used in the ESR study on the formation and decay of radical species during surface fluorination of polyethylene, as reported here. The treatment reaction was carried out inside a dedicated quartz vessel with an internal diameter of 0.5cm and length of 20cm using oxygen-free fluorine at the temperature of liquid nitrogen (T = 77K). The quartz reaction vessel was coated with PTFE to minimise the amount of $RO_2^{\bullet}$ radicals formed by the undesired side reactions of the polymer with, for example, surface-adsorbed oxygen, and in order to inhibit the reaction of fluorine with the quartz surface. A 30mg sample of LDPE in fibrous form was then placed in the quartz vessel. The vessel was then evacuated, placed inside the resonator of the ESR spectrometer, cooled to a constant temperature of 77K, and filled with fluorine to a pressure of 0.12 bar.

The ESR spectra were then monitored as fluorination proceeded. The spectra revealed the instantaneous formation of both fluoroalkyl and peroxy radicals, thus clearly indicating that a PTFE coating was not particularly effective in preventing the contamination of the reaction vessel from oxygen and oxygen-containing species.

The kinetics relating to the accumulation of radicals are shown in Figure 10. Radical formation commences immediately following the entry of fluorine into the

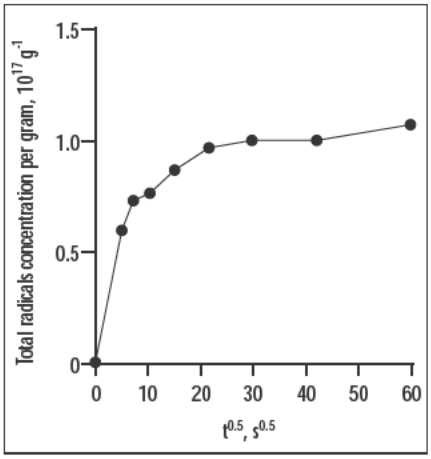

Figure 10: Total radical concentration in a fluorinated sample versus the square root of the time of fluorination as measured *in situ* at T = 77K. LDPE density = 0.918g cm^{-3}

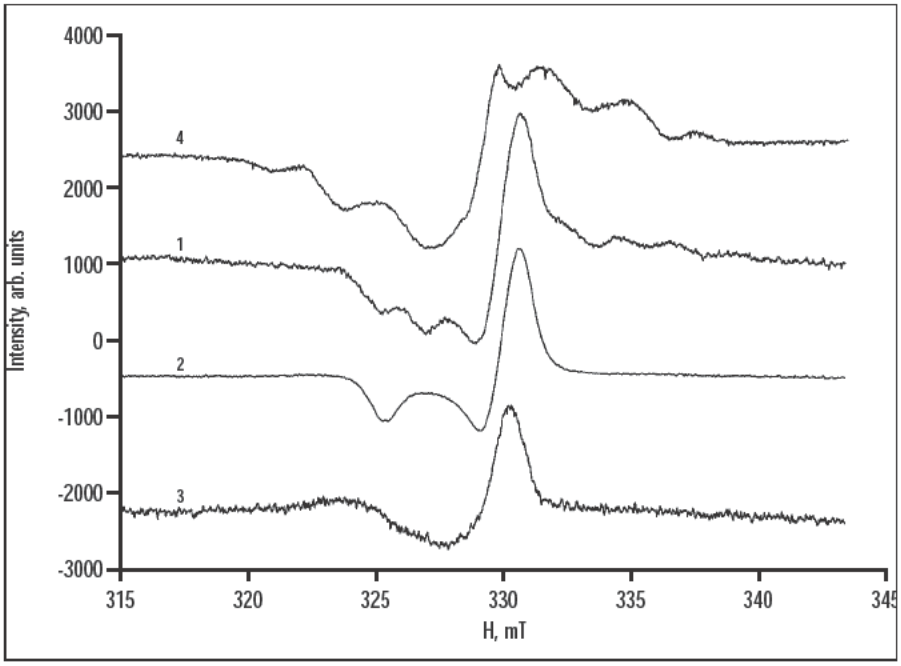

Figure 11: 1: ESR spectrum of a LDPE sample in the form of 'cotton wool' as measured 20 minutes after the insertion of fluorine into the reaction vessel. The reaction was carried out at T = 77 K; 2 and 3: spectra of the same sample which was evacuated after fluorination and oxidised. Curve 4: spectrum of gamma-irradiated (in vacuum at T = 77K) LDPE. Spectra 1, 2 and 4 were measured at 77K, spectrum 3 at 293K. The spectra were corrected with respect to the absorption of the sample before fluorination

reaction vessel and it is clearly evident that even at the temperature of liquid nitrogen, the rate of fluorination is not insignificant. In the actual experiments the concentration of the radicals soon reached a maximum concentration of around 10^{17} radicals per 1g of the total sample weight after which no further radical formation took place.

It is important to note that the above-mentioned radical concentration is an average concentration which included the fluorinated and non-fluorinated parts of the sample. ESR spectra are shown in Figure 11. Spectrum 1 was measured 20 minutes after ingress of fluorine (fluorine pressure ~0.095 bar.a and treatment temperature 77K). Spectra 2 and 3 corresponded to the same sample evacuated after fluorination and oxidised by atmospheric air and measured at 77K and 293K correspondingly. In order to identify the radicals formed during surface fluorination, samples of LDPE (density of 0.918g cm^{-3}), PVF, PVDF and PTFE were each gamma-irradiated and their ESR spectra measured. The ESR spectrum 4 in Figure 11 is the spectrum of gamma-irradiated virgin LDPE irradiated under conditions where only secondary alkyl –CH_2–CH$^{\bullet}$–CH_2– radicals were formed while the formation of allyl –CH_2–CH$^{\bullet}$–CH=CH–CH_2– radicals remained negligible.[33]

Gamma-irradiation of the fluorinated polymers such as PVF, PVDF and PTFE resulted in formation of species such as –CH_2–CF$^{\bullet}$–CH_2–, –CF_2–CF$^{\bullet}$–CH_2– and –CF_2–CF$^{\bullet}$–CF_2–. Due to the presence of F-atoms, the ESR spectra of these radicals were characterised by a very large superfine splitting. As a result, the total width of the related ESR spectra – around ~35mT – was much greater than that associated with analogue fluorine-free alkyl radicals.

Spectrum 1 in Figure 11 was measured 20 minutes after the insertion of fluorine into the reactor (p_F = 0.095 bar). The resulting spectrum is a combination of absorptions originating from the peroxy species $RO_2^{\bullet}$ and another radical which resembled the allyl –CH_2-CH$^{\bullet}$-CH=CH-CH_2- radical[33] rather than the secondary alkyl radical –CH_2-CH$^{\bullet}$-CH_2- (see reference 4, Figure 11). The super-fine splitting is too small for the fluorine-containing component formed in the irradiated PVF, PVDF or PTFE. Therefore, it is likely that during the initial stages of fluorination of the technical polyethylene, allyl radicals are formed and that these radicals initiate the subsequent fluorination of the polymer. This indicates that the fluorination starts with the abstraction of H-atoms bonded in allyl positions, and explains the fact that HDPE reacts faster than LDPE because more double bonds were found in HDPE than in LDPE. However, at T = 77K, no further reactions took place. This behaviour may be due to the existence of an activation energy barrier associated with further chain propagation and hence very low temperatures would, to a great extent, lower the rate constants of the subsequent chain reactions.

Spectra 2 and 3 in Figure 11 are the spectra of the same sample measured at 77K and 293K respectively. It is evident from the spectra, which shows typical asymmetric singlet absorptions, that all the initially formed radicals are transformed into peroxy $RO_2^{\bullet}$ radicals.

Similar results were obtained for flat LDPE films treated with undiluted fluorine for t = 100 minutes at T = 293K and 0.072 bar fluorine partial pressure (see Figure 12). The asymmetric singlet in the ESR spectrum (g-factor: $g_{\perp}$= 2.0022, $g_{||}$ = 2.0356) corresponds to the $RO_2^{\bullet}$ radical. Remarkably, the ESR spectra recorded at 77K and at room temperature are virtually coincident.

The latter result can be readily explained with the formation of secondary or 'middle' peroxy $RO_2^{\bullet}$ radicals such as ~CHOO$^{\bullet}$~ or ~CFOO$^{\bullet}$~, and terminal species such as ~CH_2OO$^{\bullet}$ or ~CHFOO$^{\bullet}$ or ~CF_2OO$^{\bullet}$. The spectra of 'middle' and 'end' radicals measured at 77K should be similar because of the 'frozen' (restricted) rotation around the polymer chain, which results in similar g-factor components were thus also similar (see Figures 11 and 12). When measured at room temperature, the spectra of 'middle' and 'end' radicals should differ from each other. The unrestricted rotation of the 'end' $RO_2^{\bullet}$ radical around the C–O bond and the axis of the polymer chain results in an averaging of the anisotropy of the g-factor and hence results in a totally symmetric singlet spectrum. As the rotation of the 'middle' $RO_2^{\bullet}$ radical around a C–O bond and

axis of a polymer chain is restricted, the g-factor is averaged only partially, and the spectrum becomes an asymmetric singlet. The detailed examination of the spectrum measured at room temperature leads to the conclusion that the majority of the radicals are 'middle' radicals. This indicates that disruptions of the polymer chain in LDPE treated under conditions similar to that of industrial 'off-line' processes are practically absent. The same experiment (insertion of fluorine into the reaction vessel at T = 77K) was carried out at a lower fluorine pressure (ie ~0.011 bar), and again a mixture of peroxy and alkyl/allyl radicals were detected. Subsequent heating of the reaction vessel to room temperature resulted in the termination of the peroxy radicals in less than 15 minutes. This can be regarded as confirmation that those peroxy radicals had a carbon-hydrogen character (ie $-CH_2-COO^{\bullet}-CH_2-$ or similar) because fluorocarbon peroxy radicals are known to have significantly greater lifetimes.[34]

Kinetics of the termination of long-lifetime radicals

LDPE density 0.918g cm^{-3}

Polymer films were fluorinated at T = 293K and stored in appropriate glass vials at liquid nitrogen temperature. Subsequently the ESR spectra were measured. The sample was then allowed to heat up to room temperature (T= 291K). Then the ESR spectra were measured again at 77K and compared with spectra obtained at low temperature measurements. In all measurements, both peroxy $RO_2^{\bullet}$ and perfluoroalkyl radicals were detected. However, the majority of the radicals were found to be of the peroxy type. The experimental conditions are summarised in Table 2.

The kinetics of radical termination at T = 293K are shown in Figure 11. It should be noted that a radical half-life $t_{1/2}$ (ie the time interval required for a decrease in radical concentration by a factor of 2) was close to between five and six hours.

LDPE density 0.926g cm^{-3}

The procedure for the treatment and testing of polymer films is described above and the experimental conditions are summarised in Table 3. The kinetics of radical termination at T = 293K are shown in Figure 11. It should be noted that the half-life for radical termination $t_{1/2}$ was close to between four and four and a half hours.

It is evident that the direct fluorination of LDPE generated a high concentration of long-lifetime radicals. In the experiments described here radical concentrations between $3{\cdot}10^{19}$ to $5{\cdot}10^{19}$ radicals per cm^3 of fluorinated polymer were determined. This means that roughly ~0.3% of the monomeric units of fluorinated LDPE contained radicals – mainly peroxy $RO_2^{\bullet}$ radicals. The average half-life-time of these radicals was four to six hours at room temperature. A decrease of both fluorine partial pressure and treatment time resulted in a small decline in concentration of the long-lifetime radicals.

Two types of peroxy $RO_2^{\bullet}$ radicals can be formed: in the middle of a chain ('middle radicals', $\sim CHO_2^{\bullet}\sim$ or $\sim CFO_2^{\bullet}\sim$), and at the end of a chain ('end radicals', $\sim CH2O_2^{\bullet}$ or $\sim CHFO_2^{\bullet}$or $\sim CF_2O_2^{\bullet}$). To distinguish 'middle' and 'end' radicals, the following experiment was carried out. A LDPE sample was treated with a F_2/O_2 mixture to form $RO_2^{\bullet}$ radicals. The ESR spectra of the treated LDPE samples were measured at a temperature of 77K and 293K. It was found that the spectra were similar because of restricted rotation and the g-

Table 2: Concentration of radicals in LDPE treated under different conditions

Sample no	*Fluorine pressure (Torr)*	*Treatment time (minutes)*	*Maximum concentration of radicals per cm^3 of fluorinated layer (radicals cm^{-3})*	*Percentage of peroxy $RO_2^{\bullet}$ radicals (%)*
LD2-E1	73.5	15	$5.2{\cdot}10^{19}$	80–90
LD2-E2	73.5	30	$2.8{\cdot}10^{19}$	80–90
LD2-E3	73.5	60	$2.6{\cdot}10^{19}$	80–90

Table 3: Concentration of radicals in LDPE treated under different conditions

Sample no	*Fluorine pressure (Torr)*	*Treatment time (minutes)*	*Maximum concentration of radicals per cm^3 of fluorinated layer (radicals cm^{-3})*	*Percentage of peroxy $RO_2^{\bullet}$ radicals (%)*
LD1-E2	147	85	$4.0{\cdot}10^{19}$	80
LD1-E3	88.2	85	$3.0{\cdot}10^{19}$	85
LD1-E4	147	45	$3.3{\cdot}10^{19}$	80
LD1-E5	88.2	45	$2.5{\cdot}10^{19}$	95
LD1-E6	147	15	$3.7{\cdot}10^{19}$	95–100

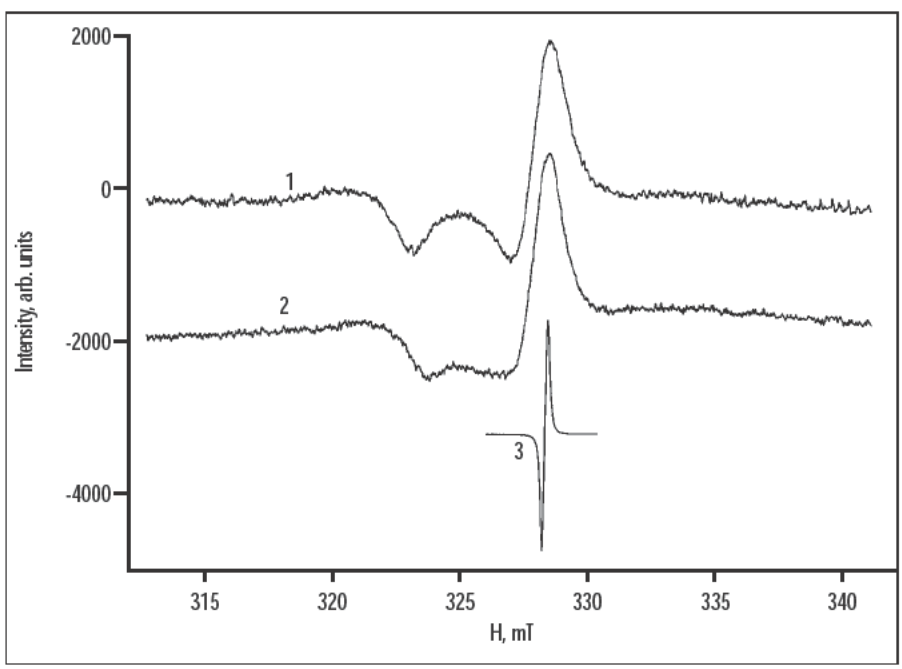

Figure 12: ESR spectra of LDPE samples in the form of a flat film fluorinated at room temperature. Treatment conditions: undiluted fluorine, p_F = 0.072 bar, fluorination time t = 100 minutes at T = 293K. Spectra 1 and 2 were measured at 77 and 293K respectively. 3: DPPH spectrum (g = 2.0036). The spectra were corrected with respect to the absorption of the sample before fluorination

Table 4: Measured concentration of double bonds and CH_3 groups in virgin LDPE and HDPE

Polymer	*Relative concentration of double bonds (moles of double bonds per moles of the main polymer unit)*					*Amount of CH_3 groups per 1000 C atoms*
	Trans-vinylene –CH=CH–	*Vinyl –CH=CH_2*	*Vinylidene $R_1R_2C=CH_2$*	*Conjugated diene –CH=CH–H=CH–*	*Total concentration of double bonds*	
LDPE density 0.918g cm^{-3}	$1.1 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$	$6.5 \cdot 10^{-4}$	0	$0.87 \cdot 10^{-3}$	24.2
HDPE no 1	$0.93 \cdot 10^{-4}$	$1.9 \cdot 10^{-3}$	$1.4 \cdot 10^{-4}$	$1.9 \cdot 10^{-4}$	$2.2 \cdot 10^{-3}$	3.7
HDPE no 2	$0.64 \cdot 10^{-4}$	$1.9 \cdot 10^{-3}$	$0.37 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	$2.2 \cdot 10^{-3}$	3.9
HDPE no 3	$1.2 \cdot 10^{-4}$	$2.4 \cdot 10^{-3}$	$0.87 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$2.9 \cdot 10^{-3}$	3.9
HDPE no 4	$0.67 \cdot 10^{-4}$	$2.5 \cdot 10^{-3}$	$0.56 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$2.9 \cdot 10^{-3}$	2.5
HDPE No.5	$0.52 \cdot 10^{-4}$	$1.4 \cdot 10^{-3}$	$0.26 \cdot 10^{-4}$	$1.6 \cdot 10^{-4}$	$1.6 \cdot 10^{-3}$	4.1

factor components were also found to be similar (ie $g_{||} = 2.033$ and $g_v = 2.001$) (see Figure 12). When measured at room temperature, the spectra of the 'middle' $\sim CF_2–CF(OO^\bullet)–CF_2\sim$ and the 'end' $\sim CF_2–CF_2–OO^\bullet$ radicals differed from each other. The reason is that unlimited rotation of the 'end' $RO_2^\bullet$ radical around the C–O bond and the axis of the polymer chain resulted in an averaging of the anisotropy of the g-factor and hence resulted in a totally symmetric singlet spectrum. On the other hand, rotation of the 'middle' $RO_2^\bullet$ radical around a C–O bond and the axis of the polymer chain would be restricted, the g-factor would thus be averaged only partially, and the spectrum would be an asymmetric singlet. Through examination of the spectrum measured at room temperature (see Figure 12, asymmetric singlet), it is possible to form the conclusion that the majority of the radicals were 'middle' radicals and that disruptions of the polymer chain within this polymer were also practically absent.

The kinetics of elementary reactions – Summary

(a) The process of LDPE fluorination is a radical process.
(b) Initiation of the reaction takes place via the reaction of molecular fluorine with C-H bonds and not via the dissociation of molecular fluorine.
(c) Both peroxy long-lifetime $RO_2^\bullet$ and fluororadicals are formed within the fluorinated layer in large concentrations. The amount of peroxy radicals exceeds the amount of fluororadicals.
(d) Termination time (ie the time required for a reduction in the amount of radicals by a factor of 2) of long-lifetime radicals for LDPE is relatively large and is around four to six hours. Hence additional modification of the polymer surface can be arranged via grafting of monomers containing double bonds.

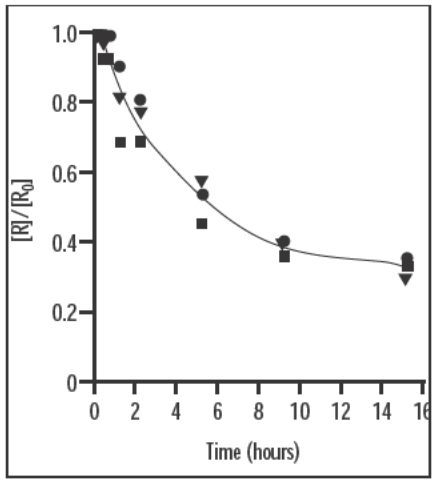

Figure 13: Ratio $[R]/[R_0]$ ([R]-concentration of radicals at time t, $[R_0]$–concentration of radicals 12 minutes after completion of fluorination) versus storage time t in the case of LDPE of a density of 0.918g cm^{-3}. Circles: LD2-E1 (see Table 3); squares: LD2-E2; triangles: LD2-E3

(e) The amount of scissions in LDPE treated under industrial conditions is negligible.

Preliminary schematic of the elementary reactions

As mentioned above, the fluorination of LDPE can be regarded as a radical process. In addition, another important conclusion concerning the initiation stage of the fluorination process can be made. The initiation stage (ie the formation of carbon-hydrogen radicals) proceeds even at liquid nitrogen temperatures (see above). This implies that the initial reaction step proceeds with almost zero activation energy. The commonly proposed initiation reaction involving the dissociation of molecular fluorine $F_2 \rightarrow F^\bullet + F^\bullet$ – a reaction which is endothermic by 159kJ/mol – does not fulfil this important requirement. However, there are a number of exothermic reactions involving molecular fluorine which are more appropriate candidates for the initial reaction step.

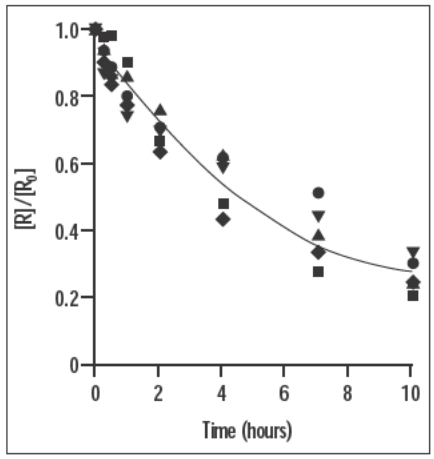

Figure 14: Ratio $[R]/[R_0]$ ([R]-concentration of radicals at time t, $[R_0]$-concentration of radicals 12 minutes after completion of fluorination) versus storage time t in the case of LDPE density of 0.926g cm^{-3}. Circles: LD1-E2 (see Table 4); horizontal squares: LD1-E3; triangles corner up: LD1-E4, triangles corner down: LD1-E5; diamonds: LDF1-E6

Among these reactions, the slightly exothermic branching reaction between F_2 and $–CH_2–$ is likely to predominate: $F_2 + –CH_2– \rightarrow F^\bullet + –CH^\bullet– + HF$.

The actual presence of a high concentration of $–CH_2–$ groups favours the $F_2 + –CH_2–$ reaction over other theoretically possible initial step reactions such as the reaction of F_2 with tertiary C-H groups or double C=C bonds. (Transvinylene, vinyl, vinylidene and conjugated diene bonds are always present in all the polyethylenes as impurities; see below):

$F_2 + >CR–H \rightarrow F^\bullet + –CR^\bullet– + HF$

$F_2 + –CH=CH–CH_2– \rightarrow F^\bullet + –CH=CH–CH^\bullet– + HF$

$F_2 + –CH_2–C(=CH_2)– \rightarrow F^\bullet + –CH^\bullet–C(=CH_2)– + HF$

$F_2 + –CH=CH– \rightarrow –CHF–CH^\bullet– + F^\bullet$

It is necessary to emphasise that, for example, the reaction between F_2 and double bonds, tertiary bonded hydrogen or weakly bonded allylic hydrogen may play an important role in industrial or

pre-processed polyethylene in which the molecular structures deviate more or less significantly from the very regular $–CH_2–CH_2–$ structure of ideal polyethylene.

FTIR spectroscopy was used to determine the concentration of C=C double bonds and $–CH_3$ groups. ($–CH_3$ groups which will hardly react with F_2 because of the very strong C–H bonds were in particular used as for polymer branching and therefore as an initiator for the presence of tertiary C–H bonds.) The extinction coefficients were taken from a number of sources.[32,35,36] The data obtained are shown in Table 4. Approximately 0.1% of the polymer units of LDPE and between 0.2% and 0.3% of the polymer units of HDPE had double bonds and the concentration of the $–CH_3$ groups was around 2.4% for LDPE and between 0.3% to 0.4% for HDPE with respect to the amount of carbon atoms. Usually such a concentration of initiators is enough to start a chain process. A similar initiation mechanism has been proposed in earlier publications by Kharitonov and Moskvin.[28,30,37]

(f) The chain propagation reactions may have an activation energy but the following exothermic processes can be proposed:

$$–CH_2– + F^{\bullet} \rightarrow –CH^{\bullet}– + HF$$

$$–CH^{\bullet}– + F_2 \rightarrow –CHF– + F^{\bullet}$$

(g) The reactions shown below are likely candidates for a chain termination reaction. Some of the reactions are highly exothermic and may cause C-C bond scission.

$$–CH^{\bullet}– + F^{\bullet} \rightarrow –CHF–$$

$$–CF^{\bullet}– + F^{\bullet} \rightarrow –CF_2–$$

$$–CH^{\bullet}– + –CF^{\bullet}– \rightarrow >CH–CF<$$

$$–CH^{\bullet}– + –CH^{\bullet}– \rightarrow >CH–CH<$$

$$–CF^{\bullet}– + –CF^{\bullet}– \rightarrow >CF–CF<$$

$$–CH^{\bullet}– + O_2 \rightarrow –CHOO^{\bullet}–$$

$$–CF^{\bullet}– + O_2 \rightarrow –CFOO^{\bullet}–$$

$$F^{\bullet} + F^{\bullet} + \text{polymer} \rightarrow F_2 + \text{polymer}$$

The absence of 'end' peroxy radicals indicates that the chain scission does not occur.

Conclusions

1. The fluorination of polyethylene proceeds via a branched chain-radical mechanism following an induction period.
2. Initiation of the reaction likely takes place via the reaction of molecular fluorine with C-H bonds and not via the dissociation of molecular fluorine.
3. Fluorination results in a replacement of hydrogen atoms with fluorine atoms, but the fluorination inside the fluorinated layer is not complete.
4. The fluorination of polyethylenes is a diffusion-controlled process. This indicates that the rate of formation of a fluorinated layer is limited by the rate of penetration of fluorine through the fluorinated polymer layer into the untreated layer. The fluorinated and untreated layers are separated by a very thin transient boundary layer where the majority of the chemical reaction takes place.
5. The rate of formation of a fluorinated layer increases with fluorine partial pressure and temperature and was not observed to be affected by the presence of He and/or N_2 in the fluorinating mixture.
6. There is practically no correlation of the fluorination rate with the actual density of the HDPE or with the presence of additives such as carbon black.
7. The rate of fluorination of HDPE significantly exceeds that of LDPE.
8. The fluorination rate of PVF is almost identical to the fluorination rate of LDPE.
9. PVDF cannot be fluorinated even at temperatures as high as 430K and/or under UV irradiation.
10. The presence of oxygen (even in trace amounts, ~0.1-0.2 volume %) results in the formation of C=O-containing groups and leads to chain scission. Those groups are hydrolysed under the action of moisture into –COOH groups.
11. Long-lifetime peroxy $RO_2^{\bullet}$ and fluororadicals are formed inside the fluorinated layer in large concentrations. The amount of peroxy radicals exceeds that of fluororadicals. The termination time (ie the time necessary for the amount of radicals to decrease by a factor of 2) of the long-lifetime radicals is around four to six hours.
12. It is mainly middle peroxy radicals that are formed under treatment conditions close to those used in industrial processes. Therefore, the amount of scissions in LDPE treated under industrial conditions is negligible.

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Exhibit A-2

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Optimization of HDPE direct fluorination conditions by XPS studies

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Abstract

A fluorination reactor was designed and built in the laboratory. The optimal conditions of fluorination within the reactor were selected by X ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) analysis of fluorinated surfaces of a film and a plaque of pure high density polyethylene (HDPE). This reactor was used to post mould fluorinate plaques and films of a range of mixtures of virgin and recycled HDPE with and without (re)introduction of additives. The ability to be fluorinated has shown no dependence on the composition virgin/recycled HDPE.

Comparison of in line and post mould fluorinated samples showed that fluorine concentration profile in depth is thinner in the in line fluorinated sample when compared with the post mould fluorinated sample, though the fluorination degree in the extreme surface is larger in the in line fluorinated sample. This is attributed to a migration of lower surface energy chain blocks towards the surface in the material at high temperatures, which is the case in the in line fluorination, hindered in the post mould fluorination where maximum temperature is below the melting point to keep the macroscopic shape. The additives played a minor role in the ability of the surface to be fluorinated.

Keywords: HDPE surface; HDPE recyclate; Direct fluorination; XPS

1. Introduction

The low and selective permeability of polymers to many fluids, gaseous or liquids, is of great importance in a great number of applications, such as packaging films, electrical cables, textiles, protecting clothes, fuel tanks, membranes, etc. Fluorocarbon resins are very well known polymers having just that property.

In many applications, however, there is a need to combine a high hydrophobicity and oleophobicity with bulk mechanical and rheological properties different from the ones in fluororesins. One of the solutions, in many applications, is to fluorinate just the polymer surface. Among the methods of surface fluorination usually reported in literature, we can cite treatment in a carbon tetrafluoride (CF_4) plasma [1,2], segregation to the surface of especially designed fluorinated molecules [3] and direct fluorination achieved by using a flow of fluorine gas (F_2), pure or diluted into an inert gas, impinging on the surface [4]. A specific example of this last method is used in the European plastic fuel tank industry where the low permeability to hydrocarbons and the other main components of fuel is assured by the fluorination of the inner walls of the tanks and will be here called "in-line" fluorination [5]. For this case, the direct fluorination is made during the blowing of the tank, i.e. at high temperature. For "post-mould" direct fluorination, i.e. fluorination of a piece of plastic after moulding, some designs of reactors are reported in the literature [6]. This kind of fluorination has many industrial applications and can be particularly useful in laboratory conditions to understand the role of all the components of the polymer (namely the additives) on the quality of the fluorination layer, thickness, homogeneity and amount of fluorine. This is particularly useful in the case of the increasing use of HDPE recyclate from fuel tanks where the evaluation of the *fluorability* (ability to be fluorinated) of the recycled material compared with the virgin material is an important parameter to decide whether reuse in the same application is possible.

Many techniques are used to study the composition and properties of the fluorinated layer [7].

One of the most powerful, given its specificity to the surface, is X-ray photoelectron spectroscopy (XPS). With its capability to make qualitative and quantitative elemental analysis and to detect the chemical environment of each element through the "chemical shift", it can provide very complete chemical information about the 10 20 first layers of a flat surface.

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One of the limitations of XPS is the degradation that X-rays may induce in organic materials especially in halogenated species, as is the case in fluorinated surfaces. This limitation may be important in the case where information about the elemental concentration as a function of depth is needed. Another problem associated with XPS analysis of polymer surfaces originates from the low electrical conductivity of samples, leading to surface charging. These two problems were thoroughly discussed elsewhere and solutions were presented to minimize them [8].

The action of fluorine on the surface topography must also be considered. Pitting phenomena induced by direct fluorination have been reported [9]. This implies that the analysis of the topography of the surface by scanning electron microscopy (SEM) is very important to ensure that the surface is uniform after fluorination.

In this work, we present a study of polyethylene surfaces, modified by direct fluorination, using X-ray photoelectron spectroscopy and scanning electron microscopy. XPS data are treated in an original way according to a methodology presented elsewhere [8], which provides a good way of assigning XPS C1s components even if the absolute binding energies cannot be determined.

2. Results and discussion

2.1. Selection of fluorination conditions

In order to choose effective conditions for laboratory fluorination, tests with a film of pure HDPE provided by Solvay were performed. Varying parameters were fluorine content in gaseous flow (from 0.013% (v/v) to 0.09% (v/v)), time of exposure (from 5 to 20 min) and temperature (from room temperature to 97 °C).

The extent of the fluorination was assessed by XPS, measuring the global F/C atomic ratio computed from the F1s and C1s peak areas and also the F/C atomic ratio computed from the C1s region [8]. The ratio between these two parameters, here called F/C ratio, gives a qualitative indication of typical dimensions of fluorine density depth profile. XPS peak fitting, was performed using Voigt profiles 50% lorentzian. For C1s region, full width at half maximum (FWHM) was constrained to be the same for all the components. The value obtained for FWHM in the samples here presented was around 2 eV. For the F1s region, a peak ~2.4 eV wide was fitted for all the samples. In Fig. 1, XPS C1s and F1s spectra for two different samples are shown as an example. EF3 was fluorinated for 5 min at a temperature of 47 °C with a gaseous flux containing dry nitrogen and 0.02% (v/v) of fluorine ($[F_2] = 0.02\%$) and EF19 was fluorinated for 20 min at a temperature of 97 °C with $[F_2] = 0.064\%$.

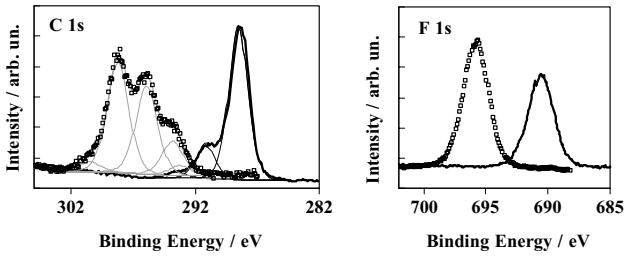


Fig. 1. XPS C1s and F1s spectra for two samples: ( ) one fluorinated for 5 min with $[F_2]$ 0.02% (v/v) and 47 °C (sample EF3); (□) another one fluorinated for 20 min with a $[F_2]$ 0.064% (v/v) and ~97 °C (sample EF19). Fitted components to C1s region are shown in grey for EF 19 sample and in black for EF 3 sample. Binding energies are not corrected for charging effects. Spectra were normalized to the same baseline. C1s region for pure virgin HDPE is not shown for figure clarity sake but it has a single peak [10].

The peak fitting to regions F1s and C1s yields parameters contained in Table 1.

In sample EF3, the charging shift is easy to compute since the most part of the carbon is bound to CH_2 far from the fluorine neighbourhood and we can attribute to it the binding energy of 285 eV [10]. We can, then, identify two peaks corresponding to carbon bound to fluorine: one 2.7 eV shifted from the CH_2 peak (at 287.7 eV) and the other

Table 1
Peak assignment and area % for C1s peak for samples in Fig. 1

	EF3 (t_F 5 min; $[F_2]$ 0.02 vol.%; T 47 °C)		EF19 (t_F 20 min; $[F_2]$ 0.064 vol.%; T 97 °C)	
	ΔBE* (eV)	Area %	ΔBE* (eV)	Area %
CH_2 (in a fluorine poor neighbourhood)	402.2	79.6	402.5	3.9
CH_2 (in a fluorine rich neighbourhood)			401.9	14.2
CF	399.5	17.1	399.8	35.0
CF_2	397.2	3.3	397.5	43.2
CF_3			395.2	3.7
Global F/C	0.28		1.54	
F/C (C1s)	0.24		1.33	
F/C ratio**	1.16 ± 0.05		1.17 ± 0.05	

Global F/C atomic ratios and F/C computed from C1s region as well as their ratio, are also presented.
* ΔBE BE_{F1s} BE_{C1s}.
** F/C ratio (global F/C)/(F/C (C1s)).

5 eV shifted (at 290 eV). Their identification is based on BE differences between F1s and C1s peaks [8], the first corresponds to CF groups and the second one to CF_2 groups. Both Fig. 1 and Table 1 show that the sample exposed to a flux richer in fluorine (sample EF19) has a more extensively fluorinated surface as shown by the global F/C ratio and by the atomic percentage of fluorinated carbons. The F/C ratio = (global F/C)/(F/C (C1s)) is also included. As shown in reference [8] its deviation from unity gives an indication of the existence of a fluorine profile decreasing with depth, having a typical dimension, l, <100 Å. In fact, for an exponential schematic profile for fluorine density ($n_F \propto \exp(-x/l)$, n_F being the bound fluorine density in depth), a flat surface and assuming a constant carbon density, we have Eq. (1), [8]:

$$\text{F/C ratio} = \frac{\text{F/C}}{\text{F/C(C 1s)}} = \frac{\lambda_C + l}{\lambda_F + l} \quad (1)$$

where $\lambda_C = 31.2$ Å and $\lambda_F = 20.5$ Å are the effective attenuation length of the C1s and F1s photoelectrons, respectively. This shows that if $l \gg l_C$ that ratio tends to 1 and when $l \to 0$, F/C ratio approaches 1.52.

Values obtained in Table 1 show that for these two films, the fluorinated layer is rather homogeneous and thicknesses are very similar. If the assumptions about the fluorine density profile shape and the flatness of the surface are correct, it appears that the typical dimension of the fluorinated layer ranges from 30 to 70 Å.

In Fig. 2, the global F/C ratios obtained by XPS as a function of temperature, F_2 contents on the flow, and time are shown.

It can be concluded that the extent of the fluorination is greater for higher temperatures but it seems to attain a plateau around 85 °C. It must be noted that, with this kind of sample (HDPE film) and this type of reactor, the study is limited to a maximum temperature of ~100 °C due to the melting point of this material (132 °C [11]) and to the highly exothermic character of the fluorination reaction ($\Delta H_r = -399$ kJ mol^{-1} [12]). We verified that for a fluorine content in the flow entering the reactor, [F_2], below 0.02% (v/v), for a time of fluorination, t_F, below 15 min and for a temperature of the reactor ≤50 °C, the global F/C atomic ratio is <1. This ratio rises for longer times of exposure to the gaseous flow, higher temperatures and higher concentrations of F_2. Fixing the time parameter at 20 min and increasing [F_2], it was possible to obtain a global F/C ratio near 1.6, with [F_2] = 0.064% (v/v) at 97 °C. The optimisation of experimental conditions was recalibrated for commercial samples from CIBA. These samples were in the form of plaques, allowing analysis in a larger temperature range, up to ~115 °C. The study of the influence of [F_2] on the extent

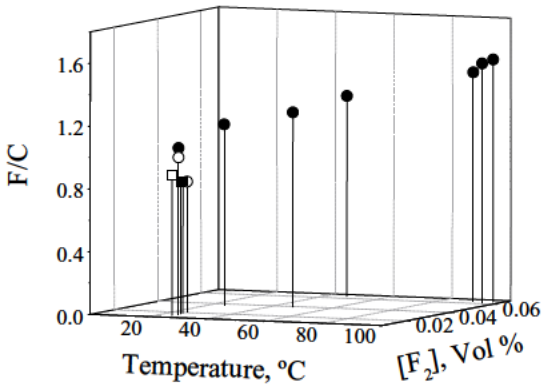
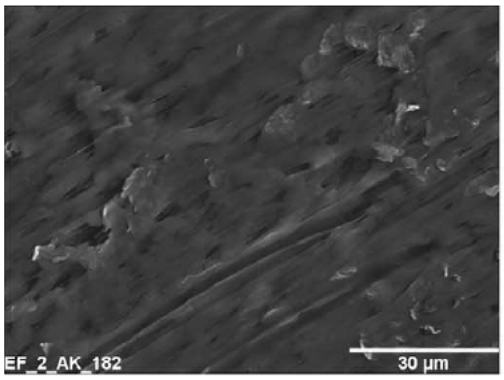
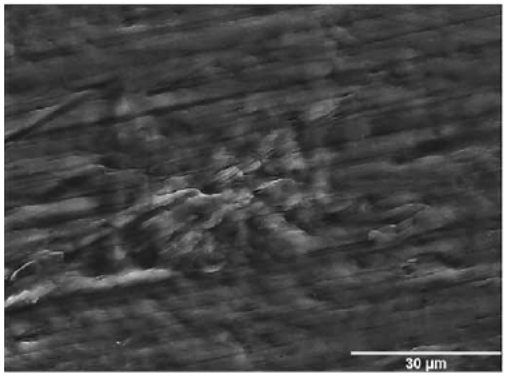


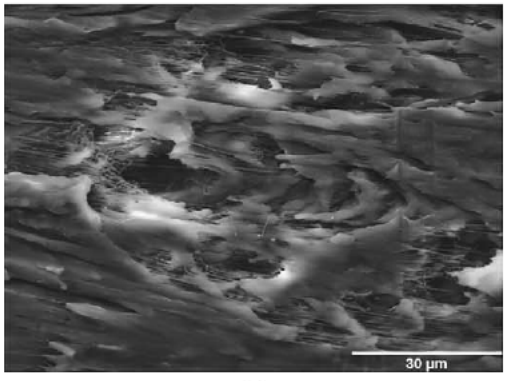
Fig. 2. Evolution of the relative amount of fluorine with three experimental parameters: the reactor's temperature, the fluorine gaseous concentration entering the reactor and the time of fluorination (□) 5 min; (■) 10 min; (○) 15 min; (●) 20 min.



(a)



(b)



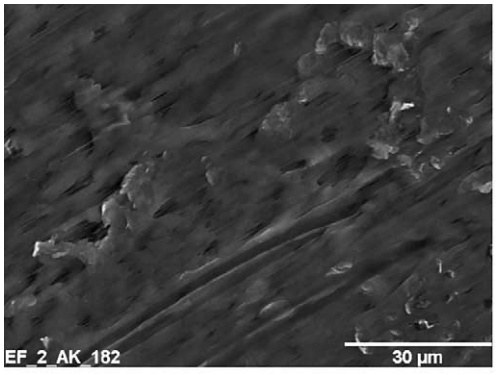
(c)

Fig. 3. SEM images for three plaques post mould fluorinated for 20 min at 90 °C, with [F_2] volume percentages of (a) 0.06; (b) 0.08; (c) 0.09.

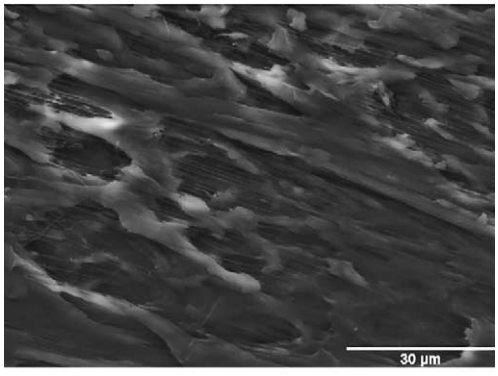
of the fluorination was limited to the contents of fluorine in the mixture ($N_2 + F_2$) we used (0.09% (v/v)). With $[F_2] = 0.09\%$ (v/v) a F/C ratio 10% higher than with 0.06% (v/v) was obtained. However, a fluorine gaseous concentration that did not exceed 0.065% (v/v) was chosen. In fact, the images obtained by SEM (Fig. 3) of three samples, fluorinated with an increasing content of F_2: 0.06, 0.08 and 0.09% (v/v), show that the surfaces are severely damaged, showing some pitting effect or even melted zones. These topographic changes become more evident for higher $[F_2]$. For that reason, a limit around 0.06% (v/v) was established, in order to keep some uniformity after the surface treatment together with a good degree of fluorination.

This large effect of fluorination on surface topography, led to analysis by SEM of two samples with the same base composition, the same surface treatment, before and after X-ray irradiation. The result is shown in Fig. 4 for two fluorinated samples at ~90 °C, for 20 min and $[F_2] = 0.06\%$ (v/v).

Images in Fig. 4 were obtained from two different pieces of a same sample, since after SEM analysis, due to the gold coating on the surface, the same piece of the sample cannot be analysed by XPS. Therefore, for the X-ray doses here used, the similarity of the images shows that the chemical degradation of the surface, already shown in reference [8], is not accompanied by a topographic degradation in spite of the release of F_2 and/or HF from the surface during irradiation. It was also verified that the central portion of the sample (placed at the centre of the reactor) was less fluorinated than the peripheral regions. In what follows the peripheral regions are compared. From this study, the following conditions of fluorination were used for the ''real'' samples: $T = 95$ 105 °C; $[F_2] = 0.064 \pm 0.002\%$ (v/v); $t_F = 20$ min.



(a)



(b)

Fig. 4. SEM images for two post mould fluorinated samples at ~90 °C, for 20 min at $[F_2]$ 0.06% (v/v) (a) before X ray irradiation; (b) after X ray irradiation for 120 min.

2.2. Correlation between resin formulation and surface fluorination ability

The characteristics of a fluorinated layer depend on the fluorination method itself, on the chemical structure of the polymer and on the possible reintroduction of additives needed to restore the chemical, mechanical and/or rheological properties of a polymer at the end of its lifecycle. In order to evaluate the ability of samples with different amounts of recycled material to be fluorinated, samples were fluorinated under the same laboratory conditions ($T = 75 \pm 2$ °C; $[F_2] = 0.062 \pm 0.002\%$ (v/v); $t_F = 20 \pm 1$ min) and analysed by XPS. To ensure that the fluorination conditions were exactly the same for all the samples, they were placed in a circle around the centre of the reactor, fluorinated simultaneously, and then kept under nitrogen atmosphere prior to analysis. Samples, under the form of plaques were mixtures of virgin HDPE without any additive and HDPE recyclate with an additive (0.5% (w/w) of Recycloblend™, an additive from CIBA). Compositions ranged from 100% virgin HDPE to 100% HDPE recyclate.

The elemental quantitative analysis of C1s and F1s regions acquired at a take-off-angle relative to the surface (TOA) of 90° shows that, within the experimental error, the relative amount of fluorine does not change with the amount of recycled material present in the sample (Fig. 5).

The average global F/C is around 1.46 and average F/C (C1s) is 1.34. The average value for F/C ratio is therefore, 1.1. All these values are close to the optimal obtained for virgin HDPE films at the same temperature, time and $[F_2]$.

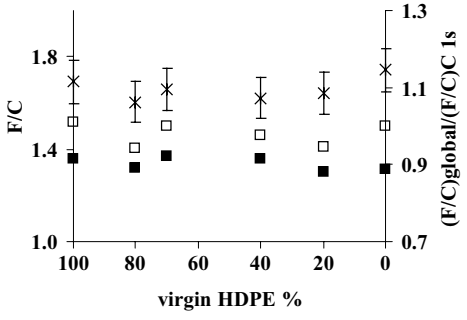


Fig. 5. Relative amount of fluorine in samples with different % of virgin HDPE: (□) global F/C atomic ratio; (■) F/C ratio computed from C1s region; (⊗) F/C ratio (defined in the text).

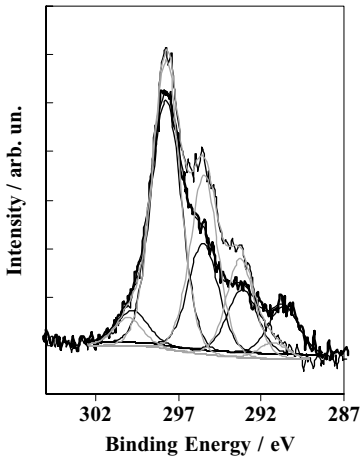


Fig. 6. XPS C1s region for a sample fluorinated in line (bold line) and another "post mould" fluorinated (thin line). Fitted components are in black for the in line sample and in grey for the post mould one. Binding energy was not corrected for charging effects. Spectra were normalized to the same baseline.

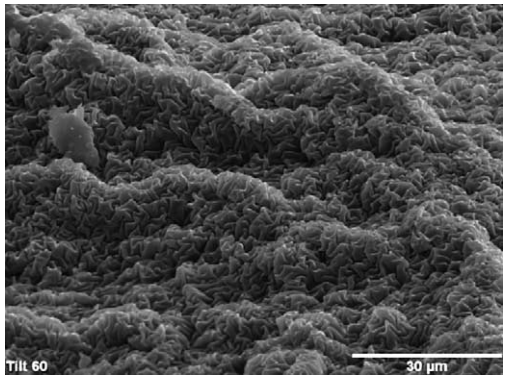


Fig. 7. SEM image of an in line fluorinated sample.

2.3. Post-mould versus in-line fluorination

The elemental analysis of the samples treated by post-mould fluorination and the analysis of the samples fluorinated "in-line" indicated that the F/C ratio was always larger in the latter ones but the nature of the fluorinated groups was essentially the same as can be seen in Fig. 6 and Table 2.

The global F/C is different in the two samples though the F/C (C1s) is the same. This yields different F/C ratios, the distance from unity being larger in the in-line fluorinated sample. This means that the fluorine composition is less uniform in depth than in the post-mould sample. A possible explanation is as follows: though the diffusion of fluorine is larger in the in-line fluorination because the HDPE is a melt, the diffusion of the lower energy surface components towards the extreme surface is also larger. The result is a fluorine concentration profile less uniform, richer in fluorine at the extreme surface of the in-line fluorinated sample, but also a much more wrinkled surface as shown by SEM in Fig. 7.

With such a rough surface, it is impossible to perform angle resolved X-ray photoelectron spectroscopy (ARXPS) studies to obtain further information about the fluorine concentration profile. The segregation of the lower energy surface components explains also why the in-line fluorinated sample is richer in (CF_2)-groups than the post-mould.

Another difference between the two samples arises from the peak at low binding energy; in the in-line sample it is 404.5 eV from the F1s peak whereas in the post-mould it is 403.9 eV. This means that the lower binding energy C1s peak is 0.6 eV lower in the in-line fluorinated sample than in the post-mould. This means that, in the in-line sample, that peak corresponds to unreacted carbon black (BE = 284.4 eV), which migrates towards the surface before the sample cools. Apparently, in the post-mould fluorination, the surfacial carbon black reacts with fluorine and the temperature within the reactor is not high enough to allow for the migration of unreacted carbon black towards the surface. Degradation studies of the in-line fluorinated sample show that the peak at 284.4 eV disappears with the degradation by X-ray irradiation. This could be due to a reaction of the remaining surfacial carbon black with the fluorine and hydrogen resulting from the degradation. Since the F1s peak always shows just one component, fluorine binds mainly covalently to sp^3 atoms in the carbon black. Therefore, respective spectra, both in C1s and F1s regions,

Table 2
Peak assignment and area % for C1s peak for samples in Fig. 6

	In line		Post mould	
	ΔBE (eV)	Area %	ΔBE (eV)	Area %
CH_2 (in a fluorine poor neighbourhood)	404.5	9.6	403.9	2.5
CH_2 (in a fluorine rich neighbourhood)	402.0	12.7	402.0	16.1
CF	399.6	21.6	399.8	29.3
CF_2	397.4	49.6	397.5	47.4
CF_3	395.3	6.4	395.2	4.6
Global F/C	1.73		1.52	
F/C (C1s)	1.40		1.38	
F/C ratio	1.24 ± 0.05		1.10 ± 0.05	
CF_2/CF	2.3		1.6	

Global F/C atomic ratios and F/C computed from C1s region, as well as their ratio, are also presented.

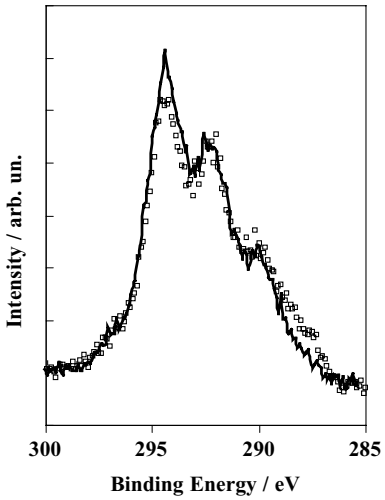


Fig. 8. XPS C1s region for two post mould fluorinated samples of a mixture of 70% virgin plus 30% recyclate HDPE: one readditivated with Recycloblend^{TM} (0.5% of the recyclate material) (bold line) and another one without any readditivation and washed with cyclohexane to remove any traces of previous additives (empty squares).

overlap with those for fluorinated polymer. Otherwise, if fluorine was largely adsorbed, or intercalated in the carbon black or bound to graphitic sites, other F1s components would develop [13]. Also the global F/C atomic ratio as a function of time, similarly to the procedure for a post-mould fluorinated sample in reference [8], was fitted with a function of the type $F/C = a + b\exp(-t/t_0)$ where t_0 is the characteristic time of degradation. The value obtained for t_0 was 230 min, compared with 250 min for the post-mould fluorinated sample. This is also evidence that the fluorine concentration profile is thinner in the in-line fluorinated sample when compared with the post-mould fluorinated sample.

2.4. Role of the introduction of additives

Mechanical and rheological properties of the mixtures of virgin and recycled HDPE, demand a reintroduction of additives. In this study, the role of that readditivation on the ability of the surface to become fluorinated was also studied.

Fig. 8 shows that the role of additivation is not very large but it may not be zero; the sample with reintroduced additives has a slightly larger atomic percentage of (CF_2)-groups and a smaller percentage of unfluorinated sites.

3. Conclusions

SEM images showed that beyond a fluorine concentration in the gaseous flow $[F_2] = 0.06\%$ (v/v), severe corrosion effects appear, pitting being clearly visible in the surface. The extent of the fluorination was greater for greater temperatures but it seems to attain a plateau around 85 °C. Fluorination degree, measured by global F/C atomic ratio also increases with time attaining saturation at around 20 min.

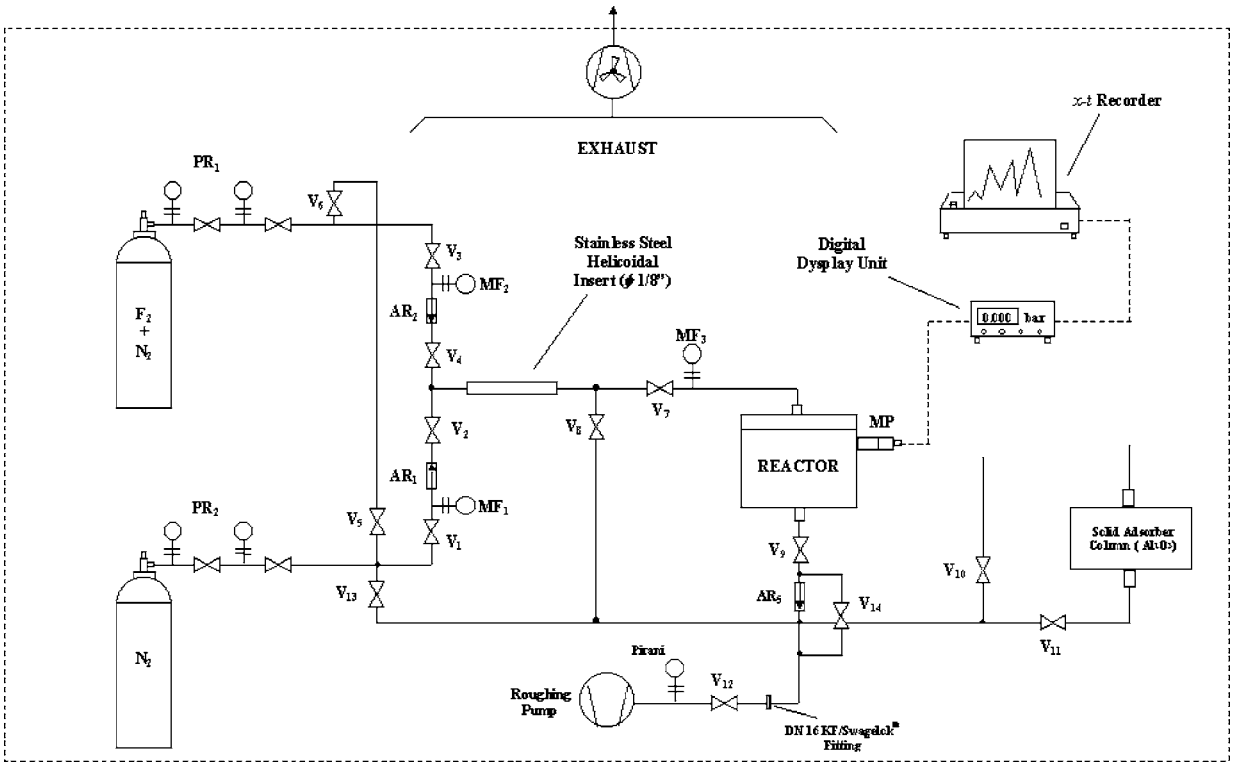
The *fluorability* does not seem to be affected by the composition virgin/recycled HDPE, as both global F/C and F/C (C1s) are identical within experimental error. Therefore both the chemical composition and the fluorine density profile in depth are identical for all compositions.

Both the value of F/C ratio (global F/C)/(F/C (C1s)) and the characteristic time of degradation show that the in-line fluorinated sample has more intensely fluorinated extreme layers but fluorine density profile in depth is thinner in the in-line fluorinated sample than in the post-mould fluorinated sample. The additives showed a minor role in the ability of the surface to be fluorinated.

4. Experimental

Materials were supplied by Ciba and by Solvay. Samples of a range of mixtures of virgin and recycle high density polyethylene (HDPE) with and without (re)additivation were provided by Ciba. Pure virgin HDPE film was supplied by Solvay. All the samples except one contain carbon black (0.2%, w/w). Samples were supplied under the form of films and/or plaques and were fluorinated and analysed as received. A few samples fluorinated in-line were also supplied. The post-mould fluorination was performed in a home-made fluorination line for use under flow conditions (see Scheme 1).

A commercially available mixture of fluorine (F_2) and nitrogen (N_2) 0.09% (v/v) in F_2, purchased from Air Liquide, was used. The composition of the mixture reaching the reactor was varied by mixing pure nitrogen with the 0.09% (v/v) fluorine mixture through a stainless steel serpentine (diameter = 1/8 in.), lined up with the pipeline. The dimensions of the serpentine were chosen to meet the conditions of a turbulent flow regime in order to improve the mixture. The final gaseous fluorine concentration, $[F_2]$, entering the reactor is determined measuring the pressures and flows from the two gas sources: $[F_2] = [Q_1/(Q_1 + Q_2)] \times [F_2]_0$. Q_1 is the feed flow from the $N_2 + F_2$ line, Q_2 is the feed flow from the N_2 line and $[F_2]_0$ is the concentration of fluorine in the mixture bottle. The pressure reducers, type DLRS and DIRS, used to adjust accurately the pressure of the gases that feed the fluorination line, were supplied by air liquide. The mass flowmeters, with a range of 3 45 l h ^{1} N_2, were Fischer & Porter Mod. D10A6142 Purgemaster, supplied by Tecnilab Portugal. The pressure inside the reactor was measured by an industrial pressure transducer, Mod. P675-2 bar, and displayed in a digital display conditioner type CD420, both furnished by Air Liquide. The pressure sensor placed at the entrance of the roughing pump was a Pirani PVD8 digital vacuum gauge. The fluorination reactor was cylindrical with a height of 5 cm and a radius of 5 cm allowing the fluorination of surfaces with 60 cm^2. By-products, consisting mainly of



Scheme 1. Fluorination line.

hydrogen fluoride, passed through a purification system before being vented to the atmosphere. The gas waste purification system had two elements: a solid absorber column of activated Al_2O_3 (Alcatel, ref. 068779), followed by an alkaline solution of KOH (Riedel-deHaën, assay: min. 85%). All the valves, the electropolished stainless steel tubes and remaining accessories that compose the apparatus were purchased to Air Liquide.

The X-ray photoelectron spectrometer used was a XSAM800 (KRATOS) model operated in the fixed analyser transmission (FAT) mode. Pass energy of 10 eV, a power of 130 W and the non-monochromatised Mg Kα X-radiation ($h\nu = 1253.7$ eV) were used. Samples were analysed in ultra high vacuum (UHV), and typical base pressure in the analysis chamber was in the range of 10 ^{7} Pa. All sample transfers from the fluorination reactor to the analysis chamber were made under a dry nitrogen atmosphere. Samples were analysed at room temperature, at TOA = 90° 30°. Spectra were collected and stored in 200 300 channels with a step of 0.1 eV, and 60 90 s of acquisition by sweep, using a Sun SPARC Station 4 with Vision software (Kratos). The curve fitting was carried out with a non-linear least-squares algorithm using Voigt profiles. No charge compensation was used. Binding energies were corrected by using a method described elsewhere [8]. For quantification purposes, the sensitivity factors used were: F1s: 1, C1s: 0.25. They were provided by Kratos in the Vision library and checked with high molecular weight PTFE.

The scanning electron microscope was a Hitachi model S2400 SEM of 25 kV. The images presented were obtained with an acceleration voltage of 18 kV and at normal mode (secondary electrons). Due to their insulating character, samples were coated with a ~8 nm thick gold layer, deposited by high vacuum evaporation.

Acknowledgements

We acknowledge the financial support given by EU through the project RECAFUTA, Contract Number BRPR-CT98-0658 in the framework of BRITE-EURAM program. We also acknowledge our partners from Solvay, Dr. J.-M. Yernaux, and CIBA Spezialitätenchemie Lampertheim GmbH, Dr. Rudolf Pfaendner and Dr. Simon Dirk, who provided us all the samples here studied. We also acknowledge all the information given by Solvay about fluorination details.

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Exhibit A-3

High Barrier Solutions for Plastic Containers Using Fluorination Process

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Introduction

High density Polyethylene/Polypropylene granules has been successfully used in rigid containers as an efficient material for packing products from various industries and it has continuously been preferred material for development of new products or in conversion of existing products packed in materials other than plastics. Unlike other materials e.g. metals & glass etc. HDPE has all the conveniences and efficiency in terms of light weight, low cost, high stress crack resistance, having high drop impact strength, tremendous flexibility in processing/designing, some protection against moisture, solvents and gases. The only area where Polyethylene/Polypropylene has a drawback against metal or glass container is in the products where permeation and scalping is a problem. The products which typically, presently are not packed in HDPE/PP or shouldn't be packed in HDPE/PP would be chemicals ranging in different fuels, brake fluids, solvents, solvent based formulations, fuel additives, flavors and fragrances to name a few.

To overcome this drawback, ***HDPE / PP rigid containers are treated with Fluorine gas to form High Barrier Fluorinated Plastic Containers.***

Principle of Fluorination Process: Fluorination of Plastics is basically a surface modification process, which result in the substitution of hydrogen molecules by fluorine molecules, whereby bulk properties of fluorine treated plastic container / article remains unchanged.

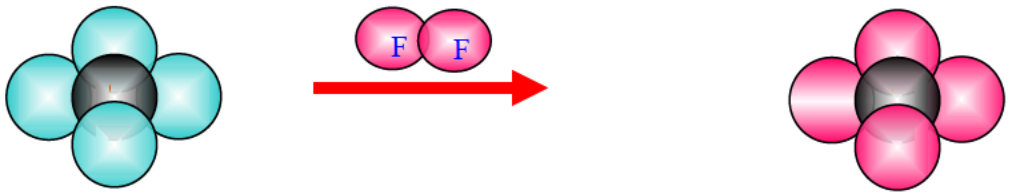
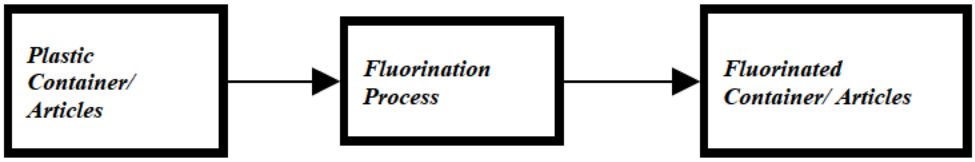
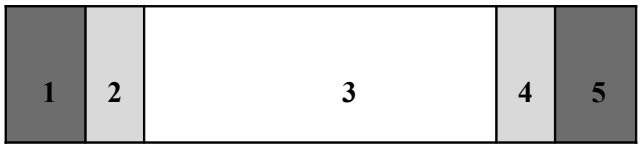


Figure 1: Fluorination Principle

The surface fluorination results in change of the surface properties of polymer drastically, while the bulk properties of the polymer remain often unchanged.

Fluorination Process





1 and 5: Fluorinated Layers
2 and 4: Boundary Transition Layer
3 : Virgin Plastic Layer

Figure 2: Section of a Fluorinated Plastic Sheet

The section of plastic container from off line fluorination process consists of (1) A fluorinated layer (2) A boundary transition layer (3) Virgin or untreated Plastic layer as shown in figure 2 from surface to inside.

In Fluorination Process the majority of the chemical reactions occur within this transition boundary layer and the majority of the physical and chemical properties such as density, refractive index, and chemical composition etc. of the polymer are mainly only changed within this layer. The layers can be schematically represented as shown below in Figure 3.

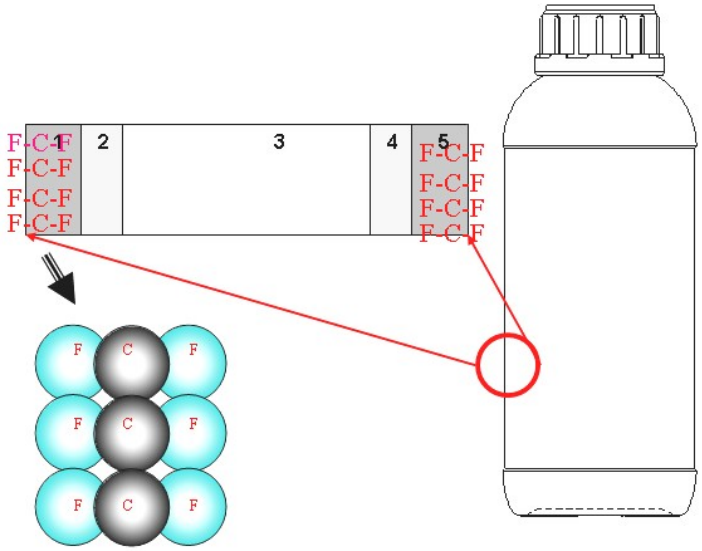


Figure 3: Layers of Fluorine on the Plastic Bottle

The fluorination changes the characteristics of the polymer in terms of polarity, cohesive energy density and surface tension. This in turn has a major effect in reducing the wetting, dissolution and diffusion of non-polar solvents relative to the polymer.

Theory of Solvent Permeation and Barrier Function

The Permeability Coefficients (P), which is a measure of the rate at which a particular solvent migrates through a polymer, is defined as

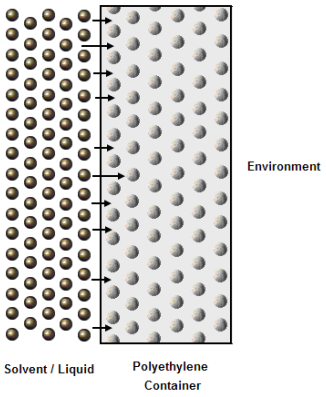
P = D x S

Where (D = diffusivity Coefficient, S = solubility Coefficient)

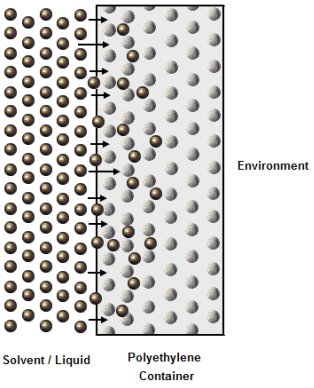
Consider the case of a solvent stored in a plastic container. The Permeation of the solvent through this container takes place due to the following steps:

Permeation in a polymer consists of four steps as given below:

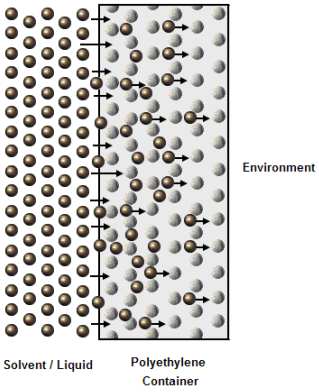
1. Wetting of the surface by the permeating liquid.



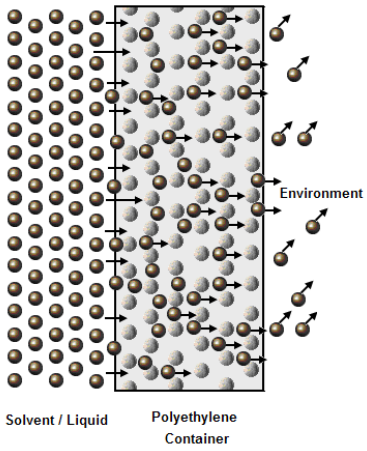
2. Dissolution of the solvent into the polymer.



3. Diffusion of Solvent through polymer and



4. De-sorption / Evaporation of the liquid through the polymer.



Hence the permeability rate of liquids through polymeric substrate / container is a function of various parameters.

The fluorination changes the characteristics of the polymer in terms of polarity, cohesive energy density and surface tension. This in turn has a major effect in reducing the wetting, dissolution and diffusion of non-polar solvents relative to the polymer as shown in figure 4.

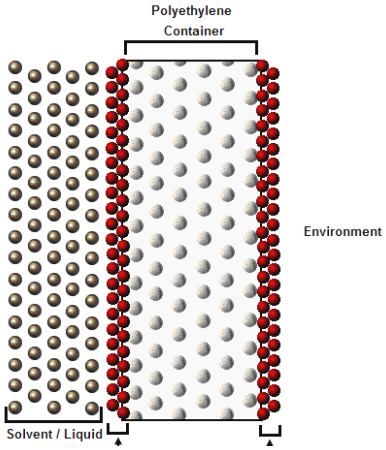


Figure 4: Cross-Section of fluorinated container wall showing the surface treatment.

Thus, fluorination is effective in minimizing the permeability of non polar solvents through a polymer surface. Since fluorination modifies only those polymer molecules near the surface, there is no measurable change in the mechanical properties such as tensile strength and impact resistance.

TESTING

Measurements of Fluorination Level:

Fluorination treatment is quantified using Fourier Transformation Infra Red Spectroscopy (FTIR). C-H bond shows peak absorption at 1440 – 1480 cm^{-1}, while C-F bond gives peak absorbance at 930 – 1320 cm^{-1}. The FTIR of untreated Polyethylene (PE) is as shown in Figure 5.

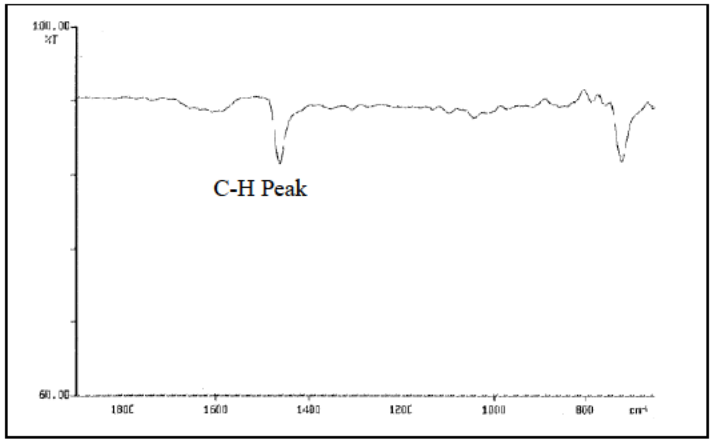


Figure 5: The FTIR of untreated Polyethylene (PE)

As seen in Figure 5, FTIR of untreated PE shows peak for C-H bond at 1440 – 1480 cm^{-1}, while the peak at 930 – 1320 cm^{-1} for the C-F bond is absent.

When Polyethylene is treated with Fluorine by direct offline Fluorination process it shows one more peak at 930 – 1320 cm^{-1} for the C-F bond as shown in the figure 6.

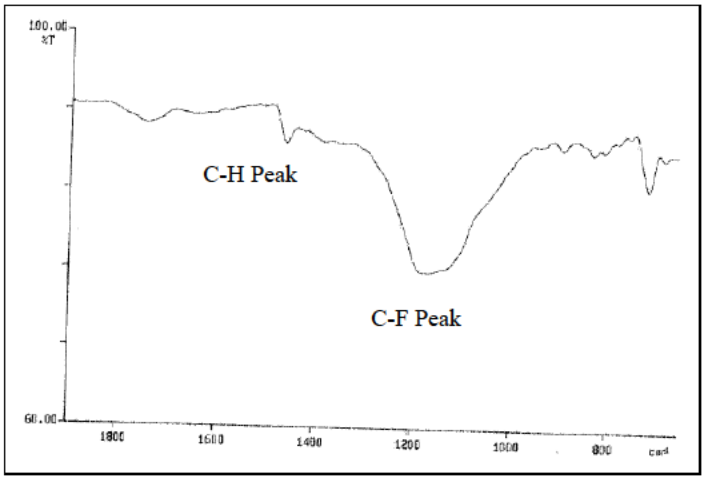


Figure 6: FTIR of treated Polyethylene.

The level of fluorination is decided based upon its % transmission ratio, which is a ratio of Peak absorbance of C-F bond and Peak absorbance of C-H bond.

$$\% \text{ Transmission Ratio} = \frac{\text{Absorbance of C-F}}{\text{Absorbance of C-H}}$$

As the fluorination treatment level is increased, the % Transmission Ratio values also keeps on increasing as shown in Figure 7. Thus fluorination treatment is quantified.

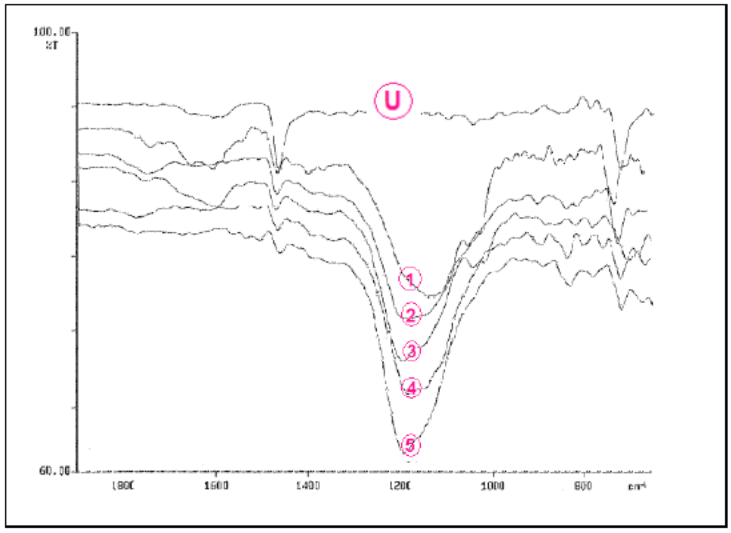


Figure 7: FTIR peaks for increasing treatment levels (U – Represents no treatment, 1-5 represents increasing Level of Fluorination)

It is very difficult to get the same and exact values for the % Transmission Ratio obtained by FTIR every time. Hence a range for these values is taken for the easy under standing of the treatment level. This range of % Transmission Ratio value is than represented in the form of values which is defined as the "***Level of Fluorination***". The conversion of range of % Transmission Ratio to ***Level of Fluorination*** is as given below in the table I.

Transmission Ratio (% T)	***Level of Fluorination***
> 12	5
> 8 & ≤ 12	4
> 6.5 & ≤ 8	3
> 5.5 & ≤ 6.5	2
> 4 & ≤ 5.5	1

Table I: The conversion of % Transmission Ratio in to Level of Fluorination.

The fluorinators world wide uses these "***Level of Fluorination***" which helps their customer as a ready reference during selection of the fluorinated containers. Every product requires different level of fluorination as they require different barrier properties. The customer takes the fluorinated container based on his barrier requirement; more is the barrier requirement or dangerous the chemical the customer goes for higher levels of treatment.

There after a customer would test these containers for the product compatibility and stability in the container. After he is satisfied with one level of treatment he will always ask for that level for his particular product package.

The level of fluorination is than generally decided by the agreement between the customer and the supplier after the supplier is satisfied that a particular level of fluorination is acceptable for his application.

Permeation Testing

The solvent permeation through containers is generally tested by an Accelerated Keeping Test (AKT) or as per IS: 2798 which involves high temperature exposure of the filled container over a period of time. Normally, exposure at 50^0C ($\pm$ 1^0C) for 28 days is considered equivalent to 1 year of normal exposure. After 28 days, a comparison of percent weight loss in the treated and untreated containers will provide an indication of permeation barrier effectiveness. Table II as shown below lists the results of permeation studies performed for various common chemicals.

Permeation Test Data for Hydrocarbon-based Solvents (as per AKT test)			
Solvent	Untreated Container	**Fluorinated Container**	Relative Barrier
	% Weight Loss	% Weight Loss	Barrier
Carbon Tetrachloride	28.26	0.05	565
Pentane	98.10	0.21	467
Hexane	61.29	0.19	323
Heptane	24.26	0.08	303
Xylene	42.52	0.21	203
Iso-Octane	4.54	0.03	151
Cyclo-Hexane	22.34	0.15	149
Toluene	61.90	0.52	119
Paraxylene	59.20	0.54	110
1,3,5 Trimethylbenzene	15.85	0.18	88
Benzene	36.68	3.65	10
Chlorobenzene	32.05	5.41	6
1,2 Dichloroethane	11.55	2.89	4

Table II: Effectiveness of Fluorination in reducing the permeability

The data in Table II proves the effectiveness of Fluorination in reducing the permeability of hydrocarbon-based solvents in HDPE containers. The above solvents are commonly used in a majority of industrial, agricultural and household products.

It should be noted that combinations of certain chemicals in a specific formulation may cause a reduction in the effectiveness of a fluorinated barrier. Therefore, it is recommended that all formulations be thoroughly tested by the method previously described prior to the final choice of packaging material.

Permeation Test data of Fluorinated Plastic Containers

Table III below gives permeation data for treated and untreated containers when filled with a wide variety of products. As can be observed, **Fluorination** process reduces the permeation losses to a great extent thereby ensuring close conformation of the product specification at the point and time of use.

Permeation Test data for Commercial Products Packaged in HDPE		
	Untreated Container (% Weight Loss)	**Fluorinated Container (% Weight Loss)**
Pesticides		
Cypermethrin 10% EC	28.90	0.12
Cypermethrin 25% EC	32.60	0.25
Chlorpyriphos 20% EC	31.44	0.22
Endosulphan 35% EC	26.12	0.15
Malathion 50% EC	23.99	0.26
Fenvalerate 20% EC	30.66	0.24
Cyflutherin EC	24.23	0.22
Lambda Cyhalothion 5%EC	22.14	0.12
Dicofol 18.5% EC	21.04	0.00
Oxflurofin 23.5% EC	27.98	0.13
Dinocap 48% EC	26.56	0.17
Quinalphos 25% EC	32.96	0.11
Ethion 50% EC	30.01	0.12
Deltamethrin 28% EC	29.11	0.14
Butachlor 50% EC	26.13	0.19
Alachlor 50% EC	27.34	0.15
Triallate 50% EC	29.66	0.13
Monocrotophos 36%SL	20.45	0.00
Paint-Related Products		
Lacquer Thinner	16.50	3.80
Mineral Spirits	15.07	0.12
Varnish	6.78	0.01
Turpentine	3.92	0.00
Automotive-Related Products		
Engine Cleaner	2.30	0.00
2-Stroke Plus Motor Oil	7.10	0.44

Table III : Permeation data for treated and untreated containers when filled with a wide variety of products.

Advantages of Fluorinated Plastic Containers

- Excellent solvent and moisture resistance
- Wide range of aggressive chemicals can be packed
- Cost efficient as compared to tin and aluminum containers
- Superior strength and durability
- Greater versatility in container design
- Better Environmental Stress Crack Resistance (ESCR)
- Lighter weight
- Easy Stackability
- Easy reprocessability
- High barrier fluorinated containers are approved by CIB (Central Insecticide Board) for a number of agrochemicals.
- Fluorinated High Barrier Containers are approved by FDA for Direct Food Contact Applications.
- **Fluorination** results in a great increase of the surface energy and hence substantial increase in adhesion properties, therefore fluorinated plastic articles can be directly printed.
- Advantages of **Fluorination** process is that it is completely dry process and plastic articles of any shape can be treated, which makes this process more versatile.
- Another significant advantage of **Fluorination** process is reduction in degree of distortion to the container wall, or paneling which is secondary effect of permeation. The paneling has a detrimental effect on container aesthetics and in turn consumer acceptance, since the container appears damaged and often has an oily surface. The Fluorinated containers exhibit minimum or no paneling compared to untreated containers.

Applications of Fluorinated Plastic Containers

Currently the most accepted packaging applications of Fluorinated Plastic Containers include insecticides, herbicides, petroleum based products like lube oil, petrol, cleaning solvents, automotive additives, penetrating oil, Degreasers, paint thinners, essential oil and pine oil.

In addition to these, a variety of products where problems of permeation, corrosion and paneling are observed in post packing period, in all these cases the possible switch over from tin, aluminum or glass to plastic offers other opportunities in terms of flexibility of shapes, closure systems and printing to the industry. We shall be too pleased to work closely with the user industry to find the most cost effective solutions to the current packaging problems.

Packaging of Pesticide, Insecticide, Herbicides chemicals

Fluorinated Plastic Containers are widely used in packaging of Pesticide, Insecticide and Herbicide Chemicals because of very high compatibility with most of the pesticides or

insecticides and absence of corrosion. Biologically active chemicals are also packed in modified Fluorinated Plastic Containers.

Flavor and Fragrance Applications

Food processors find that providing only the oxygen barrier is not sufficient, as flavor losses may render containers unacceptable. Polyolefin's materials usually lack in oxygen and flavor barrier properties. While the problem of oxygen barrier may be solved using conventional multilayer containers, the flavor still escape through these containers.

Flavors (Food Products) and Fragrances (Non-Food Products) are mixtures of many volatile complex organic compounds, usually present in ppm or even at ppb level; which impart aroma as well as taste to the food product that we eat.

Flavor Loss may occur due to three ways: absorption of flavor/ fragrance into the plastic container, due to migration of plastic additives into the product or due to oxidation of the product by ambient oxygen.

In such applications fluorinated containers offer excellent flavor barrier for a wide range of flavors. Fluorinated containers are inert and resistant to most of the organic flavor and fragrances, hence are used to pack these chemicals or solvents which otherwise would require metal or glass container.

Fluorinated flavor barrier containers are recommended for use in packaging of vegetable, fruit juice, tea, coffee, spices, and syrup flavors etc. which require very high flavor barrier properties.

Automotive Fuels and Fuel Additives

Fluorinated Plastic Containers are recommended for packaging of Automotive Fuel and Fuel Additives. The loss of the fuel such as Petrol, Diesel and Kerosene is minimum when they are packed in Fluorinated Plastic Containers.

This development improves upon present packaging material used for petrochemical products making it safer in handling as well as brings it closer to standards required in delivering stable quality products to its consumers.

Automotive Fuel Tank Applications

Today the major commercial application of fluorination technology in the developed countries is for the treatment of HDPE automotive fuel tanks.

Plastic fuel tanks have following advantages:

- Plastic Fuel tanks are typically 40-50 % lighter in weight and are less apt to explode in the event of fire.
- These fuel tanks generally have lower production costs and offer greater freedom of design, allowing more efficient utilization of dead space and thus greater fuel capacity.
- These fuel tanks meet the US federal & EPA requirements of permeation loss.

Packaging of Aromatic and Non Polar Solvents

Fluorinated Plastic Containers are widely used world over in the packaging of aromatic and non-polar chemicals.

Packaging of Solvent based Adhesives

Fluorinated Plastic Containers are very useful for packaging of solvent based adhesives as well as reactive adhesive components.

Packaging of Inks, Paints and Thinners

Fluorinated Plastic Containers are used in the Inks & Paints industries for the following solvent based applications.

- Interior / Exterior
- Wood Coats
- Varnish
- Special Coatings
- Thinners
- Melamine Finish
- Industrial Paints
- Marine – Primers
- Paint Removers
- Epoxy – Lacquers
- Paint Additives
- Thermoplastic / Heat Resistant Paints
- Acrylic Emulsions
- Synthetic Enamel Paints

Conclusions:

Fluorinated Plastic Containers and components will find various niche applications in the packaging of highly permeative, hazardous and corrosive chemicals. This technology offers great flexibility in terms of design and creativity to the end users. The recent applications in fuel tank, thinner, Petro-product, Agro, flavor and fragrance market will provide better alternative packaging options to the respective industries. With its unique advantages Fluorination process can be used in various innovative packaging applications.

About Author & Bloom Packaging Pvt. Ltd.

Mr. Bhupendra Singh a Postgraduate in Plastic Technology from UDCT is associated with Bloom Packaging Pvt. Ltd. as Manager Marketing & Business Development and is looking after the development of the High Barrier Fluorination Solutions for various chemicals.
Bloom Packaging Pvt. Ltd. has introduced new range of **BLOOM*SEAL*®** Fluorinated plastic packages for packaging applications such as Agrochemicals, Pesticides, Insecticides, Paints, Thinners, Inks, Chemical, Pharma, Food, Flavours, Fragrances, Kerosene, Diesel and Petroleum Products, which require very high barrier properties and chemical resistance properties. Bloom has its state of the art manufacturing facility at Daman and Jammu with its marketing and sales office at Mumbai.

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Exhibit B

Industrial Ecology Consultants

October 25, 2020

Ross Kulick
Sustainability Specialist | Sustainable Solutions Corporation
155 Railroad Plaza | Royersford, PA 19468

Verification Report: Inhance Technologies Enkase™ LCA

The Life Cycle Assessment (LCA) Practitioner, Sustainable Solutions Corporation, commissioned a panel of experts to perform an external independent verification of the **Enkase™ LCA** study on behalf of the commissioning organization, Inhance Technologies.

The review of the study was performed to demonstrate conformance with the following standards:

> International Organization for Standardization. (2006). *Environmental management -- Life cycle assessment – Principles and framework* (ISO 14040:2006).
>
> International Organization for Standardization. (2006). *Environmental management -- Life cycle assessment -- Requirements and guidelines* (ISO 14044:2006).
>
> International Organization for Standardization. (2014). *Environmental management -- Life cycle assessment -- Critical review processes and reviewer competencies: Additional requirements and guidelines to ISO 14044:2006*. (ISO/TS 14071:2014).

The independent third-party verification was conducted by the following panel of experts per ISO 14044:2006 Section 6.2: Critical review:

> Thomas Gloria, Ph.D.
> Founder, Chief Sustainability Engineer
> Industrial Ecology Consultants
>
> Jason Pierce[1]
> Group Leader, Circular Economy and Life Cycle Assessment
> Eastman Chemical Company
>
> David Schiraldi
> Peter A. Asseff, PhD, Professor of Organic Chemistry and Professor, Macromolecular Science and Engineering
> Case Western University

[1] Mr. Pierce performed this review as an individual consultant independent of his position at Eastman Chemical Company.

Industrial Ecology Consultants

REVIEW SCOPE

The intent of this review was to provide an independent third-party external verification of a LCA study report in conformance with the aforementioned ISO standards. This review did not include an assessment of the Life Cycle Inventory (LCI) model, however, it did include a detailed analysis of the individual datasets used to complete the study.

REVIEW PROCESS

The review process involved the verification of all requirements set forth by the applicable ISO standards cataloged in a comprehensive review table along with editorial comments. There were two rounds of comments by the reviewers submitted to the LCA practitioner. Responses by the LCA practitioner to each issue raised were resolved and acknowledged by the review panel to have been satisfactorily addressed.

VERIFICATION STATEMENT

Based on the independent verification objectives, the **Enkase™ Life Cycle Assessment, October 20, 2020** was determined to be ***in conformance*** with the applicable ISO standards. The plausibility, quality, and accuracy of the LCA-based data and supporting information are confirmed.

As the Chair of the External Independent Third-Party Review Panel, I confirm that the members of the panel have sufficient scientific knowledge and experience of polymers, packaging and the applicable ISO standards to carry out this verification.

Sincerely,

Thomas P. Gloria, Ph.D.
Founder, Chief Sustainability Engineer
Industrial Ecology Consultants

Exhibit C